VOLUME 86 NO. SA6
NOVEMBER 1960
PART 1

JOURNAL of the

Sanitary Engineering Division

PROCEEDINGS OF THE

AMERICAN SOCIETY
OF CIVIL ENGINEERS

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This Journal is published bi-monthly by the American Society of Civil Engineers. Publication office is at 2500 South State Street, Ann Arbor, Michigan. Editorial and General Offices are at 33 West 39 Street, New York 18, New York. $4.00 of a member's dues are applied as a subscription to this Journal. Second-class postage paid at Ann Arbor, Michigan.

The index for 1959 was published as ASCE Publication 1960-10 (list price $2.00); indexes for previous years are also available.

Journal of the

SANITARY ENGINEERING DIVISION

Proceedings of the American Society of Civil Engineers

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Note.--Part 2 of this Journal is the 40, 1960 Newsletter of the Sanitary Engineering Division.

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ACTIVATED CARBON REMOVAL OF HYDROGEN SULFIDE

By R. S. Murphy,[1] A. M., ASCE and I. W. Santry, Jr.,[2] F. ASCE

SYNOPSIS

The removal of Hydrogen Sulfide from an air-gas mixture presents many problems. The paper deals with the removal by one media only (activated carbon), but considers the many types of conditions that could occur, as well as the basic conditions that are created during the dynamic chemisorption.

INTRODUCTION

The problem of removing certain gases from an air-gas mixture, or the prevention of the gases from reaching the atmosphere, is becoming a more and more important problem with continued urbanization. The problem is not confined to any one industry or city, but may be found in nearly any location in which dense population exists. Gases that are nuisances, obnoxious, explosive, or toxic are the main causes of the increasing difficulties in the fields of air pollution and industrial hygiene.

There are many ways in which a gas can be eliminated from the atmosphere or from other gases; among them are adsorption, absorption, chemical reactions, and physical processes. Some of the methods have many applications, while others have a limited number of uses.

This paper is concerned with the evaluation of only one gas, hydrogen sulfide mixed with air, being removed by one media, activated carbon. In addition,

Note.—Discussion open until April 1, 1961. To extend the closing date one month, a written request must be filed with the Executive Secretary, ASCE. This paper is part of the copyrighted Journal of the Sanitary Engineering Division, Proceedings of the American Society of Civil Engineers, Vol. 86, No. SA 6, November, 1960.

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the study is basically one relating to the physical conditions that occur rather than the chemical reactions that might take place in the process.

Since hydrogen sulfide is extremely obnoxious (detectable by the nose at a concentration of 0.1 ppm) at low concentrations, and very toxic at high concentrations (maximum allowable concentration for an 8-hr period is 20 ppm), it is imperative that little or none of it reach the atmosphere that must be used for the life processes of humans, animals, or plants.

Dynamic tests were performed using three different carbons in order to determine the type of action occurring and to obtain a comparison of carbons made under varied conditions using different substances in its manufacture. These tests were run at different flow rates, filter sizes, air temperatures, humidities, and hydrogen sulfide concentrations to determine those factors that are the most important in the resulting removal process.

The removal of hydrcgen sulfide from an air-hydrogen sulfide mixture was found to be a chemical reaction rather than an adsorption process. Three factors substantiate the above conclusion. First, as the precentage of hydrogen sulfide in the total flow reached a certain level, the carbon became hot and glowed, presumably from the heat liberated due to oxidation of the hydrogen sulfide. Second, it was found that high humidities and high temperatures tend to increase hydrogen sulfide removal, contrary to adsorption theories. Third, as the total flow rate increased the carbon would remove less hydrogen sulfide, thus exhibiting the time element typical of a chemical reaction.

Although the research shows that the carbon could be of considerable value in the removal of hydrogen sulfide from such structures as large sanitary sewers and emission stacks, in which the concentration of the gas is low, it is felt that more comprehensive research should be performed before any extensive or large gas concentration application is attempted. Such factors as other carbons, non-carbon removal material, more precise instrumentation, and somewhat larger scale units are some of the variables in the problem that should be investigated.

Notation.—The letter symbols adopted for use in this paper are defined where they first appear, and are arranged alphabetically, for convenience of reference, in the Appendix.

History of Activated Carbon.—Activated carbon is an outgrowth of the use of charcoal and bone char. The earliest recognized date for the use of charcoal as a purification medium is 2,000 B.C., at which time the Egyptians filtered their water through it to remove impurities. The use of charcoal in the field of medicine has been known since 1,550 B.C. The first time the use of charcoal was recognized as a material capable of adsorbing gases was in 1773. In 1854, charcoal was suggested for use in the ventilation of sewers and described in a manner similar to that used in present day gas masks. However, it was not until World War I that activated charcoal came into being; in Europe it was used in gas masks when the German army began gas warfare. After receiving a great deal of publicity during and after World War I, activated carbon was thought to be a cure-all for a number of applications, and, after the war, a number of uses were tried for its application in industry.

Manufacture of Activated Carbon.—Over 1,000 patents are on file covering the manufacture of activated carbon. Undoubtedly, there are many times that number of different processes in existence. Basically, the material is first carbonized at elevated temperatures, allowing the distilled gases to escape from the material and leaving a very porous carbon material. Additional steps

are also used, as is evident from the number of patents, but most of these are secondary processes.

Adsorption Theory.—"Adsorption" is defined as an accumulation or concentration of a substance at a surface or interface. "Absorption" is defined as a deeper penetration in which one substance surrounds or engulfs the other substance, usually in the presence of a chemical reaction. It has been found that in many cases there is much doubt as to which of these actions is present, and, in most cases of what is referred to as adsorption, since some of the material is actually being absorbed. The term "sorption" has been suggested as a term to use regardless of which of the two actions is present or predominant.

Most theoretical work on the adsorption of gases on activated carbon is done under static conditions. This type of adsorption is carried out in a closed chamber and held at constant temperature in which the carbon is placed in the presence of the gas that is to be adsorbed. A manometer is placed in the chamber so that it can be read from the outside, and the pressure in the chamber can be noted at all times. The carbon, as it adsorbs the gas, will cause the pressure in the chamber to be reduced as the gas is adsorbed by the carbon. When adsorption ceases to take place, the partial pressure in the chamber reaches a static condition. If this static pressure, for several runs, is plotted against the cubic centimeters of gas adsorbed per gram of carbon, a straight line will be approximated on log-log paper. This line indicates that the relationship is an exponential function. The resulting equation is known as an isotherm. It might be mentioned that nearly all isotherms using activated carbon in static adsorption have positive slopes, indicating that the material is a better adsorber at greater than atmospheric pressures.

"Surface condensation" was the name first used to explain the phenomena of adsorption. This name explains quite well one type of adsorption that occurs frequently and that is now known as physical adsorption. In this type of adsorption, the gas molecules have a greater affinity for the solid surface of the carbon that they are to be adsorbed upon than they do for other molecules of the same gas. Because of this action, they will cling to the surface of the carbon rather than follow the stream path through the carbon. Even though there is a small amount of heat liberated, surface condensation is purely physical in nature.

Chemical adsorption, or "chemisorption," is also considered to be as important in the adsorption process as the physical adsorption previously mentioned. Many gases have been adsorbed on carbon, and when they are driven off, they come off as a compound of the gas and the carbon. A classical example of this type of adsorption is the adsorption of oxygen on carbon. If the oxygen is adsorbed at a relatively low temperature, it can be removed by elevating the temperature of the carbon. The gas that comes off the carbon, however, is not oxygen, but carbon monoxide, thus indicating there is a stronger bond present in the carbon than would be expected if only physical forces were present.

Chemisorption is usually accompanied by higher temperatures than pure physical adsorption, and most gases are found to be adsorbed to a greater degree by this method than by the physical adsorption.

In most actual cases, both types of adsorption take place at the same time, with the temperature rise of the removal media determining which of the two is the predominent action at any instant. Hereafter, in this paper, the term "sorption" will be used regardless of whether the process is physical, chemical, or both.

The sorption of one gas is known to be retarded by the presence of other gases even if the other gases are only slightly sorbable. Since the gas that is to be sorbed mixes with the other gases present in the system, it is more difficult for a molecule of the gas to be sorbed to reach the carbon surface; this is due to the volume relationship of the gas to be sorbed with the total volume of gases passing through the filter.

The basic properties of different activated carbons are usually somewhat different. Therefore, a carbon with one property might be a very good sorbing material for a particular gas, but because of this same property, this carbon might be a very poor sorber of some other gas. This difference can be attributed to the material from which the carbon is made, as well as the process used in its manufacture; the results of this research clearly substantiate this fact.

Activated Carbon Properties.—Activated carbon has an extremely high surface area. Carbons have been reported to have surface areas as high as 2,000 sq m per g of carbon. It is quite apparent that the higher the surface area of a carbon the higher the carbon's general sorptive powers will be.

Upon microscopic examination of the activated surface, it was found that the surface was quite smooth with a series of sunken pit-like formations covering the entire area. These pits are the entrances to the pores of the carbon.

As well as being a good adsorption media, activated carbon is also known to be an excellent catalyst in many cases. However, it is often difficult to determine, especially during tests, such as were run in this study, whether the actions were physical, or purely chemical with the carbon acting as a catalyst, or possibly a combination of the two. An analysis of the exit gases would possibly have determined whether a chemical reaction was taking place during the process, but this test was not performed since the research was concerned mainly with the physical aspects of the problem.

EXPERIMENTAL PROCEDURE

Dynamic removal was tested in this research rather than static sorption, since it was felt that the more typical uses would be of the dynamic nature rather than of the static type.

Service Time.—In this study, a "Service Time" of the carbon was determined rather than the time that the carbon took to gain equilibrium. Service Time is defined as the time from the moment the gas mixture starts to pass through a carbon bed filter until the first noticeable trace of the gas leaves the filter bed after passing through the bed. On the other hand, the "Dynamic Equilibrium Time" could be defined as that time, from the start of the test, that it takes for the composition of the gas leaving the filter to become the same as the composition of the gas entering the filter. At this point, the carbon has removed all the gas that it is able to remove under the test conditions, and the gas stream is merely flowing over the carbon bed with no action in the carbon at all during this time.

It was felt that the dynamic equilibrium time is not as important in a study such as this, since a large quantity of the gas would have escaped by the time that the system reaches this state of balance. If any hydrogen sulfide escaped, above the detectible limit, the system would not be desirable, because the condition that was to be prevented would then exist. Therefore, the time that the first minute quantity of gas appears on the exit side of the filter is the "life"

of the bed. In a practical application, this life would be the factor that would govern the operation of the system.

Instrumentation.—The system used in this research was a completely closed system, as shown in Fig. 1. The hydrogen sulfide that was used in this study was a technical grade obtained from a standard lecture bottle, and was regulated at the bottle by means of a needle valve. Immediately past this point, a two-way valve (No. 2, Fig. 1) was placed in the system. On one leg of this valve a rotometer type instrument, with a range for gases of 3 cu cm per min to 60 cu cm per min, was placed for the purpose of measuring the hydrogen sulfide flow rate. Since the concentrations of the gas were held at relatively low magnitudes, the instrument used covered the desired range quite adequately. This meter is represented as No. 3, Fig. 1.

The meter was calibrated in the laboratory for the tests by the method of air displacement of water. Hydrogen sulfide would have been the ideal gas to use in this displacement, but since hydrogen sulfide either reacts with, or is soluble in, nearly every liquid available, it was not practical to use; therefore, air was the gas used to displace the water and calibrate the meter, since air will not react to an appreciable extent with water. The resulting calibration curve for the meter agreed very closely with that supplied by the manufacturer at the higher flows, but as the flow was decreased, the meter became increasingly inaccurate. Since the meter was guaranteed only to be accurate to within 2% at the maximum scale reading, the inaccuracy was reasonable and accountable.

When the hydrogen sulfide was used in the meter during the actual tests, the rate that was read for the meter was corrected because of the difference in specific weights of air and hydrogen sulfide.

The hydrogen sulfide flow rate was measured with the gas discharging from the meter into air. When the test was started, the two-way valve (No. 2, Fig. 1) was turned so that the gas would then go through the system. Although the system pressure was somewhat less than atmospheric, no appreciable error was found to exist by measuring the hydrogen sulfide flow rate as described previously. In order to verify the accuracy, the pressure in the system was measured and, with this pressure, a correction factor was determined to be insignificant.

During some of the runs, the total amount of gas that was used was quite large, thus reducing the pressure in the hydrogen sulfide lecture bottle. This reduction in pressure caused a slight reduction of the flow rate of the gas. Because of this complication, the flow rate of the hydrogen sulfide was checked at about five minute intervals throughout each run. In order to do this check, the gas had to be turned off the system and allowed to go through the flow-meter and discharge into the air. A slight degree of inaccuracy was caused by not having the gas in the system the complete time, but the reading took only about five seconds at the longest to complete. The resulting error caused by this check reading was about 1%, a value well within the accuracy of the research as a whole.

It should be noted that the decrease in flow rate from the start of a run to the end of the run was quite uniform throughout all the tests.

Air Intake.—The air intake during all but the 100% humidity runs was through a rotometer type flow meter (No. 13, Fig. 1) that registered from 0.5 to 15 l per minute. This meter was equipped with valves on either side to regulate the flow. The fact that this gage is completely enclosed, thus allowing no losses either before or after the ball float, should also be mentioned.

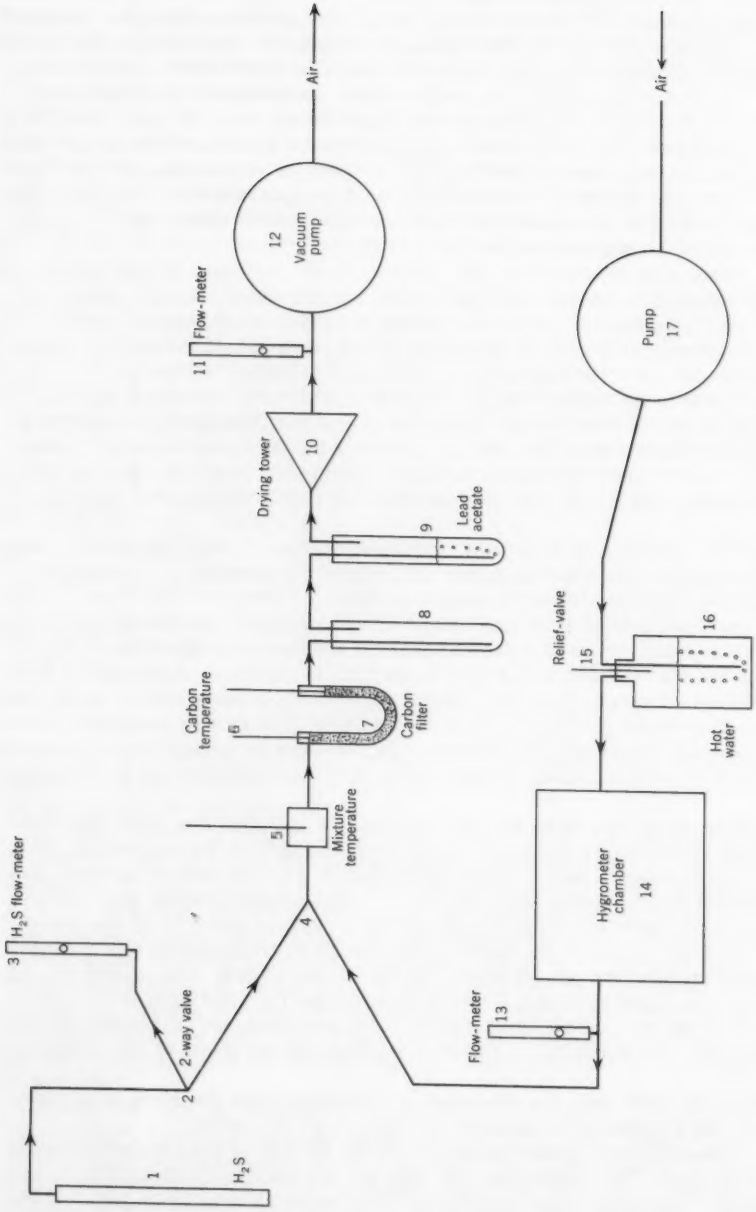

FIG. 1.—INSTRUMENTATION

Mixing.—The movement of the air and the hydrogen sulfide was effected by the vacuum pump (No. 12, Fig. 1) that pulled the mixture through the system. A wye connection (No. 4, Fig. 1) was installed connecting the hydrogen sulfide line with the air line. This connection served as a mixing point for the air and the hydrogen sulfide gas.

Since the hydrogen sulfide was never greater than 2% of the total mixture, sufficient mixing took place prior to the filter bed as determined by the Reynolds Number. At least 1 ft of tubing separated the wye and the filter, and, the flow being turbulent, good mixing should have taken place.

Mixture Temperature.—No. 5, Fig. 1 shows the relative location of the point at which the mixture temperature was determined. The apparatus used was a flask into which the flow had to pass over the bulb of a thermometer before

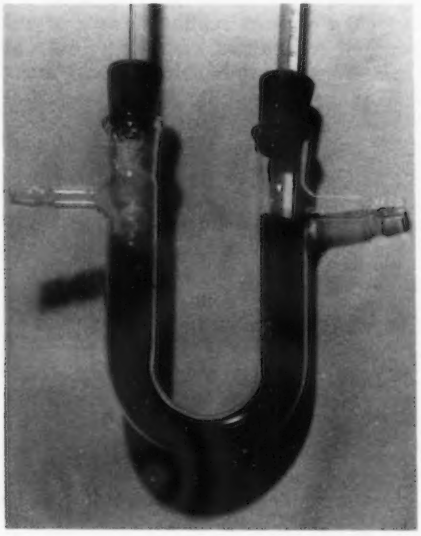

FIG. 2.—U-TUBE WITH CARBON SHOWING THERMOMETERS FOR CARBON TEMPERATURE DETERMINATION

leaving the flask. In addition to being a temperature device, this flask also acted as a point for additional mixing of the hydrogen sulfide and air.

Activated Carbon Filter.—The mixture was then brought into a calcium chloride U-tube in which the sample of activated carbon was placed. The filter is shown as No. 7, Fig. 1. Thermometers were placed in the carbon, both near the entrance and exit of this tube, so the carbon temperature could be determined throughout the run, as shown in Fig. 1, No. 6 and in Fig. 2.

As a means of trying to determine if the shape of the filter bed had any effect upon the sorptive properties of the activated carbon, a series of tests were run using a long straight tube rather than the U-tube. After finding that the filter bed shape made no difference in the results, the U-tubes were used throughout

the remainder of the tests, since these tubes were more convenient to use in the determination of the carbon entrance and exit temperatures.

Head Loss.—A differential water manometer was attached across the filter bed to see what effect the removal process might have upon the head loss across the bed. It was not the purpose of this instrument to determine what head losses might be expected if a unit were actually installed, but rather to see if the head loss across the filter changed due to gas removal taking place in the bed. The actual loss measured was somewhat greater than that caused by the carbon alone, since the manometer was tied into the system 3 or 4 in. before and after the filter bed. Since all other factors in the system remained relatively constant, the differential changes were caused by the actions in the carbon alone.

Lead Acetate Indicator.—The hydrogen sulfide was detected on the exit side of the apparatus by means of a concentrated solution of lead acetate. This solution, approximately 10 g of lead acetate in 80 g of water, is so sensitive to the presence of hydrogen sulifed that the solution turning to black is detectable when about 0.1 cu cm of the gas is bubbled through about 3 ml of the solution. The length of time from the moment the hydrogen sulfide left the filter until it was detected by the lead acetate solution was so short that no appreciable error was caused in the results of the research.

The lead acetate solution was placed in a bubbler in the system as shown in Fig. 1, unit No. 9. Unit No. 8, in the same figure, was used as a safety device to catch any of the lead acetate that might escape. In some runs, this device was placed prior to the lead acetate to protect the carbon in case of a breakdown in the equipment. However, in most of the runs, this unit was placed downstream from the lead acetate solution to protect the drying tower.

Fig. 3 shows the lead acetate solution in its clear state before any hydrogen sulfide was passed through it. Fig. 4 shows the same solution 3 sec after an air-hydrogen sulfide mixture was bubbled through it. The amount of hydrogen sulfide in the mixture that turned the solution to the deep black shade was less than one half of 1 cu cm.

Drying Tower.—A calcium chloride drying tower (No. 10, Fig. 1) was placed in the system after the lead acetate indicator as a device to protect the equipment that followed this unit. Other than a protective device, this unit served no functional purpose in the system.

Mixture Flow Meter and Control.—After the calcium chloride drying tower, another Hoke gage (No. 11, Fig. 1) was installed so that there would be a check on the total flow rate through the system. With a gage at the beginning and end of the system, it was possible for any leaks that might develop in the chain to be readily detected, since both these gages should read the same unless some air were entering between them. The hydrogen sulfide, that entered between these gages, was such a small percentage that it was unable to be detected on these gages.

Since all the air and hydrogen sulfide was being pulled through the system by means of the vacuum pump (No. 12, Fig. 1) at the end of the chain, the total flow rate was adjusted by a valve placed between the pump and the rate meter.

High Humidity Device.—During the runs that were made for high humidity determinations, another apparatus was built and attached to the entrance side of the air intake of the first flow gage (No. 13, Fig. 1). The pressure side of another vacuum pump (No. 17, Fig. 1) was used to discharge into a partially filled 5 gal jar that had hot water in it (No. 16, Fig. 1). The passage of the air through this water caused the air to pick up a great deal of moisture as well

as to become heated. The exit line of this bottle was then put into a sealed chamber (No. 17, Fig. 1) in which the air was allowed to pass across a wet and dry bulb hygrometer. A relief valve (No. 15, Fig. 1) was put on the bottle to prevent excessive pressure build-up in the system. Fig. 5 shows this protion of the system under operating conditions.

When the air reached a state of 100% humidity the test run was started. Since there were about 3 ft of tubing between the hydrometer chamber and the mixture temperature chamber, the air temperature was lowered from about 7° to 10° by the time it reached the carbon bed. With this lowering of the temperature, and with 100% humitidy condition prior to this, the humidity of the mixture at the point at which it entered the filter bed was probably near to 100%. Because of the lowering of the temperature, it is certain that the humidity was at all times just at 100%, since there was some condensation prior to the filter.

Temperature Control.—The temperature of all runs was controlled by the room temperature under which the tests were being operated. During any one run, there was never more than 1° C temperature change throughout the run.

FIG. 3.—LEAD ACETATE SOLUTION IN CLEAR STATE

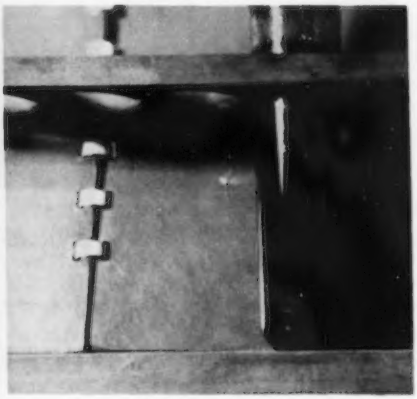

FIG. 4.—SAME SOLUTION SHOWN IN FIG. 3 AFTER H_2S CONTACT

During one series of tests, in which high air temperature was needed in large amounts, the air in the room was drawn into the system by sealing the room and heating all of the air contained therein. The temperature of the room was raised high enough so that the air entering the filter was at a temperature of 100° F.

RESULTS

The work done in connection with this research used three different types of carbon. These carbons will be designated as Type I, Type II, and Type III. The majority of the work was done with Type I carbon since this carbon was more readily available. The other carbons were used in order to determine whether their sorptive properties were the same under the same conditions of experimentation.

Properties of the Carbons

Type I.—Type I carbon is an impregnated extruded granular carbon. The total internal surface area is 1,000 - 1,200 sq m per g of carbon as determined

FIG. 5.—HIGH HUMIDITY DEVICE

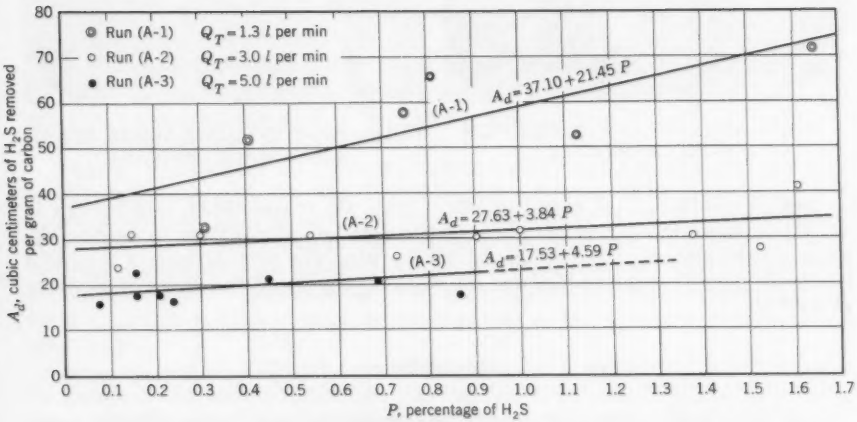
Run (A-1) Q_T = 1.3 l per min
Run (A-2) Q_T = 3.0 l per min
Run (A-3) Q_T = 5.0 l per min
(A-1) A_d = 37.10 + 21.45 P
(A-2) A_d = 27.63 + 3.84 P
(A-3) A_d = 17.53 + 4.59 P
A_d, cubic centimeters of H_2S removed per gram of carbon
P, percentage of H_2S
0 10 20 30 40 50 60 70 80
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7

FIG. 6.—H_2S REMOVED VERSUS PERCENTAGE H_2S

by the Brunauer, Emmet, and Teller (BET) method. The ash content is 5% - 10%, water solubles 2% - 5%, pH in water 9±, and the apparent density is between 0.30 and 0.50 g per cu cm. This carbon is impregnated with copper sulfate to a copper content of approximately 4% by weight.

Type II.—Type II carbon is also a copper impregnated carbon. However, the copper content of this carbon is not known, but it was assumed to be about the same as that of the Type I carbon. The total surface area by the BET method if 1,050 - 1,150 sq m per g of carbon, the apparent density is 0.50 g per cu cm, the pore volume is 0.8 cu cm c per g, the specific heat at 100°C is 0.25, the maximum ash content is 0.8%, and the maximum moisture is 2.0%. The size of this carbon is graded, according to the manufacturer, such that it will pass a 12 and be retained on a 30 U. S. Sieve. However, some of the carbon was found to pass a 200 U. S. Sieve indicating that the carbon is not capable of withstanding abrasion or rough handling in shipping.

Type III.—Type III carbon is exactly the same as Type II carbon in all respects including manufacture except that it is not copper impregnated. The tests using this carbon were run to determine whether the copper impregnation was significant in the H_2S removal process.

Effect of Variable Flow.—A group of tests were run to determine what effect a variable total flow would have upon the sorptive properties of Type I carbon. All the tests of this group were performed using the calcium chloride U-tube filter with 10 g of carbon on all runs. The data for this group of tests, Group-A, can be found in Table 3(a). A series of three runs were made with total mixture flow rates (Q_t) of 1.5, 3.0, and 5.0 l per min passing through the filter. These runs are designated as runs A-1, A-2, and A-3 respectively.

Each of these runs are made up of a series of individual tests in which the percentage of hydrogen sulfide in the total flow was varied.

There appears to be some significance between the hydrogen sulfide percentage concentration (P) and the cubic centimeters removed per gram of carbon (A_d) for the results of this group. The least square lines for these quantities were computed in an effort to determine what influence one variable has upon the other. The resulting lines can be seen in Fig. 6. Although there is some doubt as to the actual significance of this line as a predicing device, it is interesting to note that all the lines have slopes that are positive, indicating that as the percentage hydrogen sulfide increases, the carbon will remove more of the gas.

Although the lines intersect the ordinate at a point that is greater than zero, it is apparent that this is impossible, since the carbon can not adsorb any hydrogen sulfide unless it is present in the air stream. Therefore, the least square lines were stopped just short of the ordinate, since there is no evidence as to the shape of the curve between this point and the origin.

The means, standard deviations, and correlations between the percentage of hydrogen sulfide in the total flow (P) and the cubic centimeters of hydrogen sulfide removed per gram of carbon (A_d) are presented in Table 1.

As seen in Table 1, the statistical parameters are in themselves quite irregular. Run A-1 has a large standard deviation when compared to that of the other two runs of this group. However, the correlation coefficient of this run is quite large, denoting that there probably is a significant straight line through the points within the limits of the data. With this correlation coefficient, the large standard deviation seems quite reasonable, since a large standard deviation is an indication that the sample values are not from the same sample population.

The converse of the preceding is true for Runs A-2 and A-3, as can be seen in Table 1. The standard deviations of these runs are quite small, as are their correlation coefficients. Therefore, all the data in these runs could possibly have come from the same population with the variation due to experimental error only.

The increased sorptive properties might also be explained by the heat generated in the system as the hydrogen sulfide concentration became greater. A discussion of this hypothesis can be found elsewhere in this paper under the heading of "Temperature Effects upon Hydrogen Sulfide Removal."

Fig. 7 shows the relationship of the means $\bar{A}_d$ of Runs A-1, A-2, and A-3 plotted against the total mixed flow rate Q_t passing through the filter. From this line, it can be theorized that as the flow rate becomes greater the amount of hydrogen sulfide that is removed will become less. The hypothesis supports the theory as stated under the heading "Adsorption Theory." Also shown on Fig. 7 are other lines from some of the other groups of runs made during this research. These other lines support the same theory as does the line for Group A.

TABLE 1.—STATISTICAL BREAKDOWN FOR GROUP A

Run No. (1)	Mean of cu cm H_2S removed per gram, $\bar{A}_d$ (2)	Standard deviation of cu cm H_2S removed per gram (3)	Correlation coefficient of A_d and P (4)
A-1	55.1	12.5	0.772
A-2	30.8	2.5	0.488
A-3	19.4	3.1	0.411

From the data presented thus far, it is quite apparent that activated carbon might be used as a sorbent medium if the flow rates through the material are held to a relatively low value.

Effect of Variable Filter Column Length

A series of tests were made to determine what the effect on the sorptive rate per gram would be if the length of the filter were altered. In this series of tests, designated as Group-B, the total mixed flow rate Q_t was held constant throughout all runs, although the hydrogen sulfide percentage varied. The diameter of the filter was also constant, whereas the amount of carbon put into the filter was varied in the test. A series of runs were made with 5.0 g and 15.0 g of activated carbon in the filter at a total flow rate of 3.0 l per min, providing a column length of 5.5 and 18.5 cm respectively. The results of Run No. A-2, Group-A will also be used with the results of Group-B, since this run used the same carbon and the same flow rate. The tabulated results for Group-B can be found in Table 3(b).

A statistical breakdown of the results of this test are shown in Table 2. In this table, the mean hydrogen sulfide removed per gram of carbon $\bar{A}_d$, standard deviation of the hydrogen sulfide removed per gram, and the correlation between the hydrogen sulfide removed per gram A_d and the percentage hydrogen sulfide in the total flow are shown. These same parameters are also included for Run No. A-1 for comparative purposes.

The standard deviations for this group of runs is quite large, when compared to the magnitude of the mean for the same runs. Run B-1 has a large correlation coefficient indicating that this run probably has some significance when related to the percentage hydrogen sulfide in the gas stream passing through

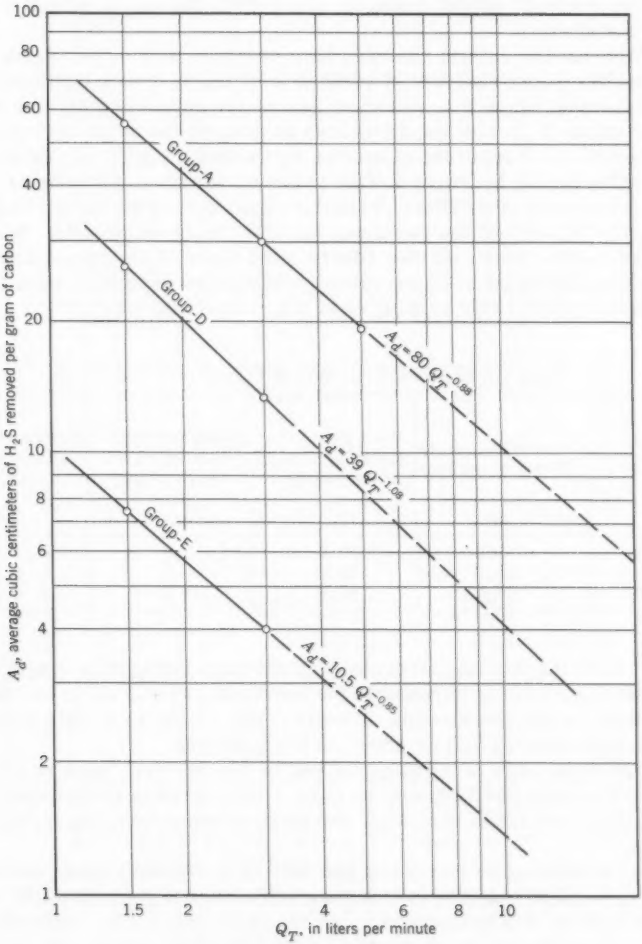

FIG. 7.—AVERAGE H_2S REMOVED VERSUS TOTAL FLOW RATE

the filter. Therefore, the high standard deviation in this run follows the general trend, as pointed out in discussion of the runs in Group-A.

The statistical parameters for Run A-2 have previously been discussed.

The significant factor in Run B-2 is the very low correlation coefficient. Upon studying the data for this run, it can be seen that Run No. B-2, 3 has a

very large value for the cubic centimeters of hydrogen sulfide removed per gram of carbon, when compared to these same quantities for the remainder of the group. The cause of this high degree of removal was not able to be determined in the laboratory at the time of the test, and no apparent errors in the instrumentation could be detected at that time. It is, therefore, not known whether this high degree of removal was caused by some error, or whether some other force or property was in action that was not in action on the other runs of this group.

The fact that the carbon removes less hydrogen sulfide per gram of carbon at the smaller filter size would seem to be a fairly unusual phenomena when first considered, since it is assumed that under approximately the same conditions, a gram of carbon should be able to remove the same amount of the gas regardless of the magnitude of carbon in the bed. Fig. 8, a plot of the mean cubic centimeters of hydrogen sulfide removed per gram $\bar{A}_d$ versus the number of grams of carbon in the filter, definitely shows that as the carbon bed becomes smaller, the amount of the gas removed also becomes smaller on a straight line relationship. Since all the filters used were of the same diameter, the relationship presented in this section could also be thought of as a function of the thickness of the filter as well as of the mass of the carbon.

TABLE 2.—STATISTICAL BREAKDOWN FOR GROUP-B

Run No. (1)	Gram of carbon (2)	Mean cu cm removed per gram of carbon $\bar{A}_d$ (3)	Standard deviation of cu cm removed per gram (4)	Correlation coefficient of A_d and P (5)
B-1	5.0	10.1	7.2	0.81
A-2	10.0	30.8	2.8	0.49
B-2	15.0	50.4	13.8	0.23

Fig. 8 shows that the line involved does not pass through the origin, as might be presumed, since it is impossible for any hydrogen sulfide to be adsorbed if there is none in the gas stream. However, the converse of this statement is not necessarily true as can be shown in the following.

Since the runs were stopped at the end of the Service Time rather than at the time of Dynamic Equilibrium, the carbon in the beds in some cases removed only part of what it could remove if the tests were carried out to the equilibrium time.

It is more difficult to remove a gas that is mixed with other gases than it would be to remove one that is in a pure state when it goes through the filter. Since this testing was performed in an air-hydrogen sulfide mixture, the removal was hampered to some degree. This retarding factor was also pointed out in the tests that had a variable flow rate. It is, therefore, hypothesized that a family of curves could be developed similar to that shown in Fig. 8 for a series of different flow rates. For a total flow rate greater than 3.0 l per min, the curves would be parallel to the one shown, but would intercept the abscissa at a point greater than the point at which the 3.0 l per min flow rate intercepts it. Also, if the flow rate were less, the line should intercept the abscissa at a point nearer to zero.

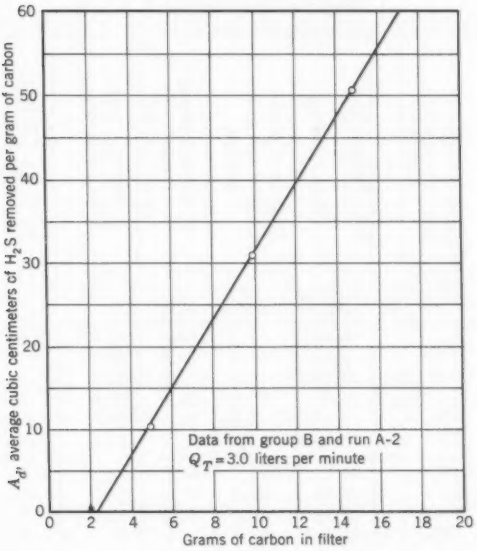
A_d, average cubic centimeters of H_2S removed per gram of carbon
Grams of carbon in filter
Data from group B and run A-2
Q_T = 3.0 liters per minute

FIG. 8.—AVERAGE H_2S REMOVED VERSUS CARBON FILTER SIZE

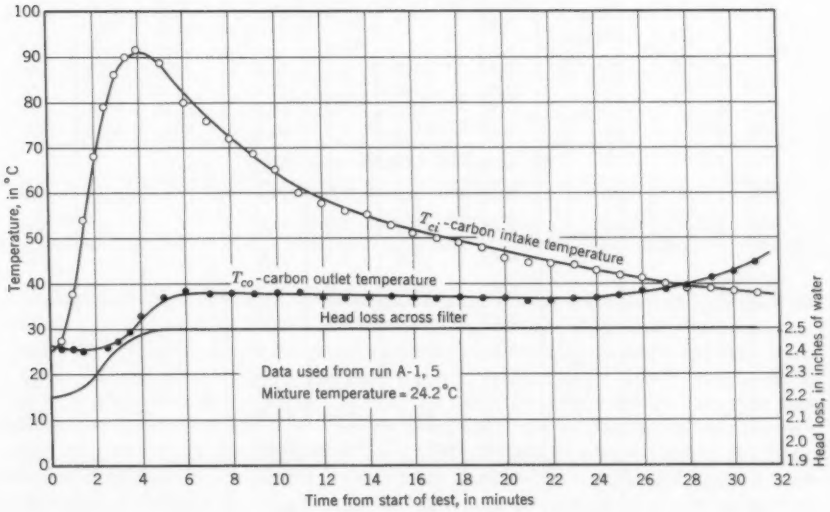
Temperature, in °C
Head loss, in inches of water
Time from start of test, in minutes
T_{ci} - carbon intake temperature
T_{co} - carbon outlet temperature
Head loss across filter
Data used from run A-1, 5
Mixture temperature = 24.2°C

FIG. 9.—CARBON TEMPERATURES AND FILTER HEAD LOSS VERSUS TIME

TABLE 3.—SUMMARY OF DATA

Test	Number	Q_t, in liters per minute	Carbon	P, Percent H_2S in Total flow Q_t	A_d, cc H_2S removed per gram carbon	T, Service time, min.	t_A, Average Mixture temp., °C.	Max. t_{ci}, Carbon Intake Temp., °C.	Max. t_{co}, Carbon Outlet temp. °C.	H, Relative Atmospheric Humidity, %
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
(a) Group-A, U-tube filter										
A-1	1	1.5	Type I 10g	0.31	32.1	69.0	24.0	43.0	28.5	40
	2			0.41	51.5	83.0	26.0	- -	34.0	32
	3			0.75	57.3	51.0	25.9	70.0	46.0	35
	4			0.81	65.3	54.0	26.0	68.0	41.5	38
	5			1.13	52.9	31.0	24.2	91.5	45.0	33
	6			1.65	71.6	29.0	24.0	119.0	48.0	30
A-2	1	3.0	Type I 10g	0.12	23.7	66.5	21.3	31.0	29.0	55
	2			0.15	31.4	70.0	24.0	37.0	32.0	43
	3			0.30	30.7	34.0	25.0	40.1	42.9	33
	4			0.54	30.8	19.0	23.0	42.0	53.0	37
	5			0.91	30.0	11.0	23.0	87.0	87.0	36
	6			1.38	31.0	7.5	25.5	108.0	68.0	52
	7			1.53	27.5	6.0	20.5	121.0	58.0	62
	8			1.61	41.1	8.5	21.0	113.0	120.0	39
A-3	1	5.0	Type I 10g	0.08	15.9	41.0	24.5	32.0	30.0	54
	2			0.16	22.6	28.0	22.5	33.0	34.0	56
	3			0.16	17.6	22.0	24.0	36.0	35.7	54
	4			0.21	17.5	17.0	24.0	35.6	38.0	58
	5			0.24	15.9	13.0	23.7	37.0	45.0	47
	6			0.45	21.2	9.5	23.0	49.5	58.0	44
	7			0.69	20.6	6.1	25.0	71.0	78.0	51
	8			0.73	25.6	7.0	24.5	55.0	72.0	73
	9			0.87	17.4	4.0	24.6	85.0	48.0	51
(b) Group-B, Straight-tube filter										
B-1	1	3.0	Type I 5g	0.19	3.5	3.0	23.4	. . .	. . .	69
	2			0.36	11.8	5.5	24.6	. . .	. . .	36
	3			0.60	7.2	2.0	24.9	. . .	. . .	43
	4			0.85	20.2	4.0	24.7	. . .	. . .	37
B-2	1	3.0	Type I 15g	0.17	47.8	138.0	24.9	. . .	. . .	37
	2			0.26	47.1	90.0	23.9	. . .	. . .	39
	3			0.57	74.0	65.0	24.0	. . .	. . .	33
	4			0.96	49.7	26.0	23.5	. . .	. . .	42
(c) Group-C, U-tube filter										
C-1	1	3.0	Type I 10g	0.35	42.9	41.0	38.8	56.5	52.0	38
	2			0.45	44.7	33.0	40.5	63.0	56.5	43
	3			0.80	33.4	14.0	37.5	67.0	64.5	36
	4			0.90	43.3	16.0	37.2	76.6	69.0	40

TABLE 3.—CONT'D

Test	Number	Q_t, in liters per minute	Carbon	P, Percent H_2S in Total flow Q_t	A_d, cc H_2S removed per gram carbon	T, Service time, min.	t_A, Average Mixture temp., °C.	Max. t_{ci}, Carbon Intake Temp., °C.	Max. t_{co}, Carbon Outlet temp. °C.	H, Relative Atmospheric Humidity, %
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
(d) Group-D, U-tube filter										
D-1	1	1.5	Type II 10g	0.74	23.3	21.0	26.7	40.0	37.5	49
	2			1.31	27.1	13.8	22.4	44.3	46.0	53
	3			2.24	73.7	22.0	24.0	51.0	145.0	50
D-2	1	3.0	Type II 10g	0.23	15.2	21.5	23.3	27.1	34.4	50
	2			0.30	12.7	14.0	23.8	29.9	39.0	50
	3			0.41	9.0	7.4	23.8	29.5	37.0	50
	4			0.61	10.9	6.0	22.8	30.0	40.0	49
	5			0.72	11.9	5.5	22.2	32.0	40.0	49
	6			1.56	10.2	2.2	24.0	34.7	48.0	50
(e) Group-E, U-tube filter										
E-1	1	1.5	Type III 10g	0.71	7.2	6.8	25.1	36.0	41.0	- - -
	2			1.30	7.8	4.0	25.1	37.5	50.0	55
E-2	1	3.0	Type III 10g	0.22	3.9	6.0	24.4	26.1	32.0	48
	2			1.19	4.5	2.5	27.1	30.1	38.0	47
(f) Group F, U-tube filter										
F-1	1	3.0	Type II 10g	0.32	52.3	55.0	25.6	45.0	40.0	100
	2			0.67	20.0	10.0	26.6	49.4	45.6	100
	3			0.74	21.2	9.5	26.0	49.6	53.0	100
	4			1.10	24.9	6.5	26.0	55.0	55.0	100

The magnitude of carbon at the point of intersection of the line on Fig. 8 is also thought to be of significance. In the filter used in this test, the minimum quantity of carbon at which removal will take place without a zero service time is 2.4 g. If any amount less than this were to be put into a filter, the service time would be zero, as some of the hydrogen sulfide would not be removed and would come through the filter. The distance that this magnitude of carbon occupies can, therefore, be thought of as the length that is needed under the conditions of this test to completely remove the residual hydrogen sulfide that does not become removed in the carbon previous to that layer. A more complete discussion of the residual gas and the mass of carbon needed to gain proper removal will be made in the next section that deals with the temperature changes taking place as the hydrogen sulfate is removed. It will be shown that the temperature increases are a direct function of the hydrogen sulfide removed, and that the temperature changes take place in a regular manner.

It must be remembered that the tests discussed in this section are for one total flow rate, one filter size (diameter), and one type of carbon. Other filter sizes, carbons, and flow rates should be tested to verify some of the "family" relationships found during this research, as it is possible that other parameters might be found that will increase the knowledge of the properties needed for a practical installation.

Temperature Effects Upon Hydrogen Sulfide Removal.—At the very start of the experimentation, it was noticed that the carbon became warm, and in some cases hot, during the sorption process. Because of this occurrence, thermometers were placed in the carbon both at the entrance and exit of the U-tube filter. Although the temperature recordings that were obtained from these thermometers can not be compared precisely from one run to another, because the bulbs of the thermometers were not set in the carbon the same distance on each run, the data obtained serves the purpose of presenting another hypothesis concerning the sorptive power of activated carbon.

At the start of a run, the temperature of the carbon will immediately start to rise in the carbon at the entrance side of the filter. As the run progressed, this temperature, designated t_{ci}, would reach a maximum and then slowly recede throughout the rest of the run. The percentage hydrogen sulfide in the air stream was also found to be a function of how great t_{ci} would become. On some runs, the carbon would become so hot that it would start to glow very brightly. This temperature was beyond the range of the thermometers used, therefore, no data could be obtained as to how great the heat actually was. This increased heat phenomena was not limited to just one test, but occurred on all runs of the experimentation in varying magnitude.

It should be pointed out that the heat never became as great on the runs having a total flow rate of 5.0 l per min as it did on those runs whose flow rate was less than this value. The reason for this occurrence is that the higher flow rate tends to act as an air cooler and does not allow the heat to build up to such a great extent by dissipating it through the bed.

The hot layer of carbon that started at the entrance to the bed traveled around the U-tube toward the exit as the test progressed. The exit thermometer temperature, too, was seen to rise quite soon after the start of the test and then remain relatively constant for most of the remainder of the run. The initial rise of the exit thermometer was undoubtedly caused by the air being heated at the start of the filter and remaining hot until after it had passed through the filter, thus providing the heat that caused the temperature to rise at the exit.

Toward the end of a run, the exit temperature would start to rise in a manner similar to that which occurred at the entrance to the carbon at the start of the run. In most cases, it was at this point that the first traces of the hydrogen sulfide started to turn the lead acetate indicator dark; this darkening indicates the srevice time and the end of the test. However, during some runs, the exit thermometer was set deeper into the carbon, and the exit temperature would then reach the same value as the entrance temperature had at the start of the run. A typical case of the temperature rises is shown in Fig. 9 for one run.

Also shown on Fig. 9 is the head loss across the filter plotted against time from the start of the test. The head loss was determined merely as a function of the time and not as an indication of how great the loss would become for any particular carbon. It was seen that the head loss rose until the time at which the maximum temperature was attained in the entrance section of the filter, at which time the loss remained constant throughout the remainder of the run.

The apparent significance of this loss is evidenced by the fact that it remained constant after the first part of the run started. The theory to explain this constant loss is that the carbon expands when it becomes heated during the sorption process, and, therefore, with the total flow rate remaining constant, the head loss is increased. When the maximum temperature is attained in the filter, the maximum head loss occurs at approximately the same time. After the temperature starts to subside, the carbon then shrinks back to its original size at the first section, while it expands at the next section in the filter.

As was pointed out in the preceding section, the temperature starts to drop immediately after attaining its maximum on the entrance side of the filter. It may be theorized that when the temperature drops in a section of the carbon all removal possible in that section has taken place, and the next section will begin its total removal process. Therefore, the process might be considered to consist of a band traveling around the filter bed, starting at the entrance and ending at the exit side of the filter at the end of the run. It was pointed out in regard to Fig. 8 that there must be a certain amount of carbon in the bed before any removal would take place. This section, or length or carbon, will be called the residual section, as it is the section that can not obtain total equilibrium with respect to the amount of hydrogen sulfide entering and leaving the section without the Service Time being zero.

Fig. 10 represents the hypothesis that is thought by the authors to be taking place in the sorption process. An air-hydrogen sulfide mixture enters the filter, and the carbon begins to rise somewhat in temperature. After the carbon has reached its maximum temperature at the entrance, a band of high temperature will begin to progress through the filter, with each increment of length presumably reaching this same maximum temperature. As the band moves, the carbon in the band will remove all the hydrogen sulfide it is capable of removing under those set conditions and leave behind it the carbon that is in equilibrium with respect to the incoming and outgoing gas in that particular section. Immediately following this high temperature band is a band that removes nearly all the residual hydrogen sulfide that was not removed in the high temperature band. This residual section is thought to be of the same size as the section determined by the intercept on the abscissa of Fig. 8. Following the residual section is that section of carbon that has only air passing through it at any instant.

Therefore, the filter bed is made up of a section that is in equilibrium with the hydrogen sulfide, an active removal section, a residual hydrogen sulfide removing section, and a section having only air passing through it. Once the moving band reaches the point at which the leading boundary of the residual section is at the exit of the filter, the hydrogen sulfide will appear in the exit stream, and the Service Time will have been reached, since a small quantity of hydrogen sulfide will escape at this point and be detected.

The high temperatures in the carbon bed are thought to be caused by the oxidation of the hydrogen sulfide forming another sulfur compound on the carbon itself. Undoubtedly, the largest amount of the hydrogen sulfide gas is removed from the flow by this process that would be termed chemisorption rather than adsorption. However, some of the gas is undoubtedly adsorbed in the strict sense of the word. Therefore, more than one process is thought to be taking place in the filter at all times.

A microscopic examination was made of some of the carbon that was "burned" on a run when the carbon glowed. It was noticed that, on the visible portions of this carbon, some very small particulate material was present. Upon comparing this to carbon that had not been used in the process, it was noticed

that these particles were not present on the unused material. The conclusion based upon the preceding facts is that the particles must be a chemical compound formed in the removal process.

There is a possibility that a strict chemical reaction is also taking place as well as the sorption processes previously mentioned. Since equipment was not available for the exact determination of what the actual cause of the hydrogen sulfide removal actions were, little is able to be said concerning these properties that are chemical in nature.

During any set of runs, it was noticed that the greatest removal took place during the test that had the largest percentage of hydrogen sulfide in the total flow. It was also noticed that, in most cases, the highest carbon temperatures

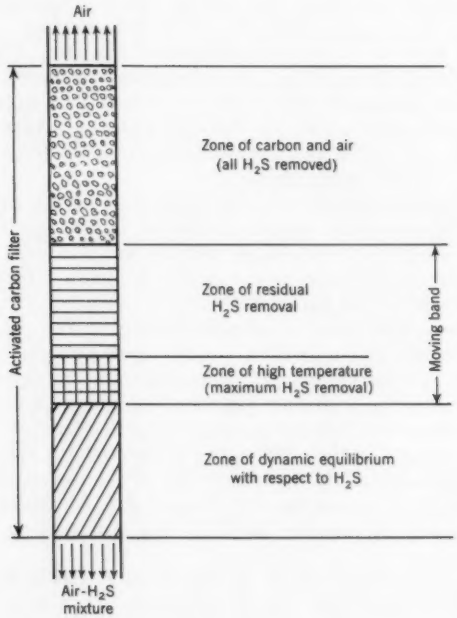

FIG. 10.—FILTER REMOVAL ZONES

also occurred during these same runs. Because of this occurrence, it may be presumed that a series of runs at high temperatures, using the same carbon as previously used, would prove beneficial to the understanding of the action in filter.

The room in which the tests were being made was warmed to a temperature of near 100° F, for one group of tests to simulate a relatively high temperature condition that might be found in the summer months in some parts of this country. The air-hydrogen sulfide mixture was, therefore, at this temperature upon entering the carbon bed during any one run.

The results of this series of tests, Group-C, can be found in Table 3(c). Since the runs used 10.0 g of Type I carbon at a total flow rate of 3.0 liters per minute, the results of this group will be compared to the results of Run No.

A-2, that was run under the same conditions, except that the temperatures of the mixture were somewhat lower.

The mean value of the cubic centimeters removed per gram of carbon in Group C-1 was found to be 41.1. The corresponding value for Run A-2 was 30.8. Therefore, the runs at an elevated temperature removed approximately 33% more hydrogen sulfide per gram of activated carbon.

The means of the mixture temperatures in runs A-2 and C-1 were 22.0° C and 38.5° C respectively, a 68% increase in temperature for run C-1.

Since the temperature of the incoming mixed flow to the filter proved to be an important factor in the amount of hydrogen sulfide that may be removed by this specific carbon, a great number of applications of a filter bed of this type might be in processes operating at an elevated temperature.

The most logical reason for the increased temperature causing a greater degree of removal could be explained by the fact that the process is really a chemisorption process to a large extent, and that heat tends to increase the chemical reactions that are taking place. An increase in heat decreases the adsorptive powers of a carbon,[2] but aids in chemical reactions, thus supporting the hypothesis that the process is one of chemical reaction.

Further study on this phase of the process is definitely needed. In order to gain a better understanding of the temperature relationships in the filter, a series of recording themocouples should be placed in the carbon bed itself so that a definite pattern could be developed for a series of different conditions and different carbons.

Another important phase of the process that should be investigated is that all conditions of the runs be held constant except for the mixture temperature. The mixture should be controlled from a low of near 32°F to a high temperature of near 200° F. With a series of runs using this information, a defitite relationship could be established for the temperature factors involved in the removal process.

Investigation of Type II Carbon.—Since Type II carbon is quite similar to Type I carbon in many respects, except that it was supplied by a different manufacturer, a series of tests was run to see if there would be an appreciable difference between the two types. The standard U-tube filter was used on these runs, as well as the same amount of carbon on all runs, namely 10.0 g. Two separate runs were made under different total flow rates. These flow rates were 3.0 and 1.5 l per min total flow. The results of this series of tests can be seen in Table 3(d). The group has been designated as Group-D.

The third run of D-1 will not be considered in the following discussion, since it has a removal value that is a great deal larger than any of the other runs in this group. A possible reason that this run was so high might be a breakdown of the equipment such as a clogged line leading into the system from the hydrogen sulfide lecture bottle or some other breakdown in the equipment.

The mean values, omitting Run D-1, 2, are 25.2 and 11.6 cu cm of hydrogen sulfide removed per gram of carbon for Runs D-1 and D-2, respectively. The means for this test are significantly lower than the means found for Runs A-1 and A-2, as reported previously. The general trend of this difference can be seen in Fig. 7, because of the smaller value of the intercept.

Extensive tests were not conducted beyond this point, since the reason for making this series of runs was to determine whether there was or was not a difference in the two carbons. Since it is felt that a definite difference has been shown, the tests were not carried out further.

The significance of the results of this series of tests is to show that, in all probability, all the carbons that are to be considered for use should first be tested to see whether they fall into the general removal level desired.

This same difference in removal properties may also be true for the same carbon obtained from the manufacturer at different times. Although no specific series of tests were made, a sample of Type I carbon was obtained from the manufacturer at a time difference of about six months from the time the first sample was obtained, and it appeared to have much less removal power than the original sample. The indication here is that close quality control has probably not been observed in the manufacture of the carbon.

Investigation of Type III Carbon.—Since both Types I and II carbons were impregnated with copper, it was felt that a carbon should be tested that was not so impregnated in order to determine whether the copper was aiding the removal. Group E, the results of which are in Table 3(e), is an attempt to determine the extent to which the copper helps the removal process.

Type II and Type III carbons are exactly the same in all respects, except that the latter is not impregnated with copper. Therefore, the results of this Group will be compared with Group D. All conditions were held as close to the same in Group E and Group D, so that a proper comparison could be made. However, the authors have no knowledge of whether or not the material was made from the same batch of raw material.

The mean cubic centimeters removed per gram of carbon for Run E-1 was 7.5 and for Run No. A-2 was 4.2. These values are considerably below those determined for the runs in Group D. Again, the reader must be referred to Fig. 7, to see these differences graphically.

For the runs at a total flow rate of 1.5 l per min, Run D-1 had 75% greater removal than Run E-1, whereas at a flow rate of 3.0 l per min D-2 had 64% greater removal than Run E-2. Therefore, copper impregnation may be considered to be a vital factor in the removal of hydrogen sulfide from a hydrogen sulfide - air mixture. The reason may be attributed to the fact that the hydrogen sulfide chemically reacts with the copper, or the copper acts as a catalyst, thus causing a chemical reaction in addition to the removal that is carried on in the process without the copper.

Effect of High Humidity.—One of the more important uses for the removal of small quantities of hydrogen sulfide would be from industrial plants discharging into a humid atmosphere such as may be found in the chemical industry or in large sanitary sewers. The series of tests run to determine what effect humidities near 100% would have upon the removal properties used Type II carbon, therefore, this group of runs will be compared with Run D-2.

Group F series of runs were run using only one total mixed flow rate of 3.0 l per min and ten grams of carbon in the filter. The results can be seen in Table 3(f).

The cubic centimeters removed per gram of carbon for Group-F was 29.6. There is one test in this group that seems to be somewhat high, this being Run F-1. If this run were omitted from the computations, the mean removal of cubic cemtimeters of hydrogen sulfide per gram of carbon would be 22.0.

Comparing the preceding figures with those determined in Run D-2, it can be seen that the high humidity created a 50% increase in hydrogen sulfide removal when using the mean value of 29.6. If Run F-1 were omitted, the high humidity would still produce a 47% greater removal rate than the lower humidities.

The apparent increase in removal in this group can not be solely attributed to sorption, because of the fact that during these runs the hydrogen sulfide is probably reacting with the moisture in the air to form a weak sulfuric acid, that, being in a vapor state, would be quite readily removed from the flow through the filter.

It is, therefore, apparent that more hydrogen sulfide may be removed from the stream with the high humidities, but it can not be said that the hydrogen sulfide is being adsorbed by the activated carbon, as the case is probably that the sulfuric acid is being adsorbed, or absorbed.

The percentage of relative humidity at which an increase in removal power takes place was not determined, although it is felt that this is an important factor in the process.

CONCLUSION

Activated carbon appears to be of some practical use in the removal of hydrogen sulfide from an air-hydrogen sulfide mixture. However, the process studied in this research indicates a number of limitations as follows:

1. Only small percentages of hydrogen sulfide can be in the air-hydrogen sulfide mixture, or the possibility of fire or explosion could develop due to the heat liberated by the activated carbon during the removal process.
2. For economic reasons, the total mixed flow rate through the filter must be kept to a minimum practical value in order to make the zone of residual removal as short as possible.
3. Due to the fact that nearly all carbons are different when supplied by different manufacturers, each individual carbon should be tested to determine its removal powers and to establish the limitations of its use.
4. The size of the filter structure might have to be of an excessive size, since the contact time is a proportional function to the hydrogen sulfide removal.

The most significant factor determined in the research was that the process was not one of adsorption, but chemisorption, since it was definitely shown that chemical reactions were taking place. This conclusion can be supported by the following:

a. The heat present in all runs of the experiment is typical of chemical reactions.
b. An increase in the heat of the mixture caused an increase in removal, contrary to adsorption theory.
c. Microscopic examination of carbon used in the process revealed solid particles on the carbon surface indicating a chemical reaction.
d. An increase in the moisture present in the air caused an increase in the removal of hydrogen sulfide.
e. As the total mixed flow rate was increased, the carbon removed less hydrogen sulfide, thus revealing the incremental time element typical of chemical reactions.
f. As the carbon bed was reduced in size, holding everything else constant, the carbon removed less hydrogen sulfide per gram.

APPENDIX.—NOTATION

The following symbols are adopted for use in the paper and for the guidance of discussers.

A_d = Cubic centimeters hydrogen sulfide removed per gram of carbon;

$\overline{A}_d$ = mean of A_d;

H = relative humidity, in percentage;

P = percentage hydrogen sulfide in total flow, by volume;

Q_t = total flow rate of air-hydrogen sulfide mixture, liters per minute;

T = service time, in minutes;

t_A = average mixture flow temperature, in °C;

t_{ci} = carbon temperature at filter intake, in °C; and

t_{co} = carbon temperature at filter outlet, in °C.

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Journal of the
SANITARY ENGINEERING DIVISION
Proceedings of the American Society of Civil Engineers

INVESTIGATION ON THE CORROSIVE BEHAVIOR OF WATERS

By Werner Stumm,[1] M. ASCE

SYNOPSIS

An interpretation is given to specific corrosion results obtained in field and laboratory investigations. The complex mutual interaction of corrosion stimulating and inhibiting factors (pH, buffer capacity, $CaCO_3$ deposition, and alkalinity) is treated.

INTRODUCTION

The objective of the study presented here was the collection of field results on the corrosive properties of different natural waters toward cast iron. Originally it was hoped to be able to correlate by means of such data the mineral composition of a water and its corrosive behavior, but it was soon realized that a statistical approach would require an excessive number of investigations, since fresh water corrosion depends on so many interdependent variables. The field investigations were supplemented by a few laboratory studies with synthetic waters.

The results obtained permit the critical analysis of concepts and theories that have been advanced within the last decades. Sanitary engineers and water supply operators have been taught that pH and calcium carbonate ($CaCO_3$) saturation are significant and important parameters for the control of corrosion. The addition of lime and soda ash to waters, in order to render the water more

Note.—Discussion open until April 1, 1961. To extend the closing date one month, a written request must be filed with the Executive Secretary, ASCE. This paper is part of the copyrighted Journal of the Sanitary Engineering Division, Proceedings of the American Society of Civil Engineers, Vol. 86, No. SA 6, November, 1960.

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alkaline and to increase $CaCO_3$ saturation index as the treatment for the mitigation of corrosion, has become a conventional practice in many water supplies. The purpose of this paper is to show that such generalized and oversimplified concepts (high pH and $CaCO_3$ saturation) are frequently not in agreement with practical experience. On the basis of the available results, the complex mutual interaction and the simultaneous influence of several parameters (pH, buffer capacity, $CaCO_3$-saturation and $CaCO_3$-deposition and alkalinity), are critically discussed.

Experimental Method.—Corrosion measurements were made on approximately 1.6 in.-by-0.6 in.-by-0.13 in. samples of cast iron with the same chemical composition as standard cast iron pipe. The specimens were ground, polished, and degreased prior to the immersion into the test water. The edges were coated with Glyptal and insulated with plastic electrical insulating tape.

The specimens were immersed in a flow cell with test water flowing over them at a constant velocity of 1.2 cm per sec. The chemical analysis of the waters used is given in Table 1. The chemical composition of the test waters remained fairly constant during the tests. In the experiments with the natural waters, the flow cell was directly connected to a water supply line. In the laboratory tests with synthetic waters, the solutions were recirculated from a 30 gallon reservoir through the flow cell by means of a stainless steel gear pump. The synthetic waters were continuously aerated, and the pH was kept constant by continuously dosing the necessary amount of CO_2 into the water by means of an automatic titrator (Beckman). The temperature was maintained at 10 (± 2)°C.

Progress of corrosion was measured by determining the weight loss of specimens that were exposed for different time intervals over a period of at least 50 days. Prior to the reweighing, the corrosion products were carefully removed from the specimens. In the tests with the synthetic waters, the gravimetric corrosion measurements were supplemented with electrical measurements of the instantaneous corrosion rate. This electrochemical estimation of the corrosion rate consists in measuring the polarization resistance in the region of the corrosion potential. The surface conditions and the corrosion behavior of the specimens is not distorted by this measuring technique so that consecutive measurements can be made with the same specimen. The electrochemical technique is a modification of a method originally developed by Skold and Larson (18).[2] The author has recently described the procedure and the theoretical principles of this method (21).

Corrosion Rates.—The extent of corrosion determined as weight loss is plotted in Fig. 1 as a function of time for all the waters investigated. In order to avoid crowding the figure, individual experimental points are given only for water No. 6 (Table 1), illustrating that experimental weight loss results can be fitted by a rather well defined curve that characterizes the corrosive properties of the water. Fig. 1 shows that weight loss of cast iron is a smoothly changing function of time of exposure. It would appear that the weight loss would asymptotically reach a constant value, but this is not the case. After prolonged periods of immersion, the corrosion reaction appears to proceed to a steady state in which the corrosion rate becomes constant. Thus, results obtained within the first 100 days of exposure at this low velocity are not representative of the ultimate steady state corrosion rate. The rate of approach to this steady state,

[2] Numerals in parenthesis thus; (1)—refer to corresponding items in the Appendix, Bibliography.

TABLE 1.—CHEMICAL COMPOSITION AND CORROSION CHARACTERISTICS OF WATERS INVESTIGATED

Number	Type[a]	Temperature, in degree C	pH	Analysis, as mp per l $CaCO_2$							$CaCO_3$ Deposition, in mg per cm^2		Saturation Index, in pH units	Buffer Capacity, mg per pH	Corrosion Rate, mg dm^2 per day				
				Analysis, mg per l															
				Ca+2	Mg+2	Alkilinity	Cl^-	SO_4 -2	Si	O	20 days	50 days			Initial	5 days	20 days	50 days	100 days
1	Sy	10	7.1	190	0	250	14	20	–	11.0	0.35	0.43	-0.40	1.92	182	37.6	5.2	1.1	–
2	Gr	9.8	7.6	185	69	245	3	20	7	11.0	3.5	3.6	+0.07	0.674	166	45	7.7	2.0	0.5
3	Sy	10	7.1	250	0	250	14	20	–	11.0	0.24	0.31	-0.25	1.92	182	54	10.4	2.3	–
4	Gr	12	7.5	158	37	180	12	–	–	2-4	–	–	-0.20	0.61	106	54	17.6	4.6	–
5	Gr	12	7.4	203	55	228	4	–	–	9	–	0.8	-0.08	1.01	150	57.3	13.0	2.9	–
6	Su	4.7	7.7	124	24	136	2	16	2	11.5	2.6	2.7	-0.40	0.33	80	53	21.8	7.7	1.6
7	Su	6.4	8.0	99	12	103	2	–	2.5	12.2	6.5	9.2	-0.20	0.14	100	59	20.8	6.6	1.8
8	Sy	10	7.0	0	0	250	14	20	–	11.0	0	0	–	2.30	125	67.9	22.2	6.4	–
9	Sy	10	8.2	38	0	83	–	20	–	11	2.4	4.6	-0.40	0.08	111	79.4	38.5	14.2	–
10	Sy	3-5	7.0	40	8	12	–	–	–	12.5	–	–	-2.5	0.11	77	65.0	42.5	22.2	10
11	Sy	10	8.3	20	0	100	14	20	–	11.0	2.5	4.8	-0.50	0.09	83.2	68.9	43.2	21.3	–
12	Sy	10	8.6	38	0	209	–	20	–	11.0	6.1	12.0	+0.30	0.22	156	96	35.7	12	–
13	Su	10	6.4	55	17	47	16	32	–	11	0.08	0.10	-1.6	0.524	105	76.3	48.9	22.9	–
14	Su	10-16	8.5	55	17	47	16	32	–	9-11	2.6	5.3	±0.0	0.045	106	87.1	53.2	25.8	10.4
15[b]	Gr	12	7.1	278	37	285	12	–	–	5-6	–	–	-0.15	2.20	142	105.5	52.4	21.5	–
16	Sy	10	8.0	0	0	250	–	20	–	11	0	0	–	0.28	208	146	66	24.4	–
17	Sy	10	8.1	0	0	150	12	20	–	11	0	0	–	0.17	182	139	71.2	29.2	–

[a] Sy = synthetic, Su = surface, Gr = ground water.
[b] 33 mg per l Hitrate and occurrence of iron bacteria.

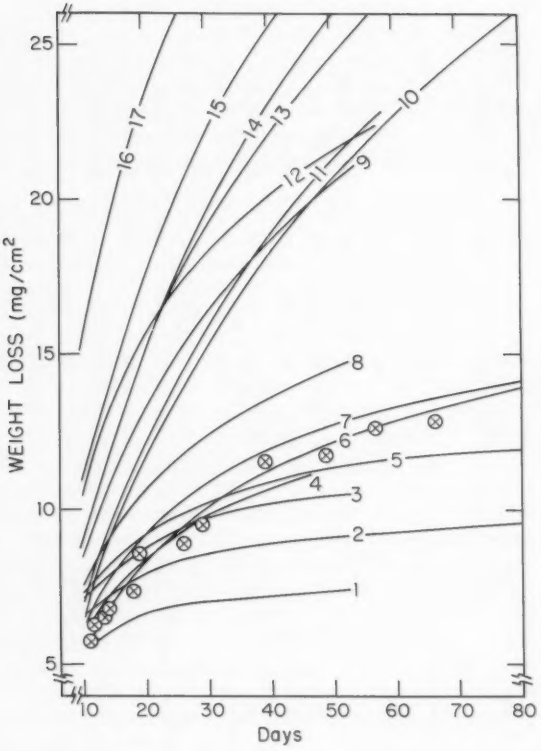
WEIGHT LOSS (mg/cm²)
Days
25
20
15
10
5
10
20
30
40
50
60
70
80
16—17
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1

FIG. 1

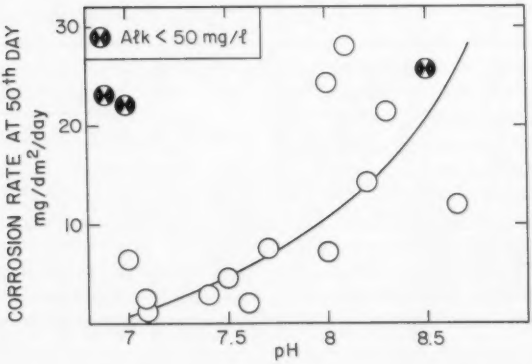
CORROSION RATE AT 50th DAY
mg/dm²/day
Alk < 50 mg/ℓ
pH
30
20
10
7
7.5
8
8.5

FIG. 2

however, is indicative for the inhibitive properties of the natural coatings and films that are formed on the iron surface by corrosion products and constituents of the water.

It should be pointed out that machines cast iron shows a different corrosion behavior that unground or tar coated cast iron. Results obtained with ground specimens are representative of the action of water on holidays or holes in the natural surface skin of iron oxide or of the tar coating that covers the interior of the pipe.

Table 1 also lists the instantaneous corrosion rates at different times of exposure. These values were computed by taking the derivative of the weight loss - time curves and are believed to be accurate within approximately $\pm$ 25%. In the tests with synthetic waters, corrosion rates have also been determined by the electrochemical method. These values were in close agreement with the values computed from the weight loss data. It is seen from this table that the initial corrosion rate does not vary appreciably for the different waters investigated. It appears that the extent of this initial rate is related to the salinity of the test waters and the concentration of dissolved oxygen. This indicates that in the early phase of the corrosion process the supply of oxygen to the cathodic regions of the iron surface and the conductivity of the electrolyte control the rate of corrosion. After corrosion has progressed for some time, significantly different corrosion rates are observed with different waters. Since most of the waters investigated have similar concentrations of dissolved oxygen, it is reasonable to assume that these differences in the corrosiveness are due to coatings and films that retard the respective cathodic and anodic electrode processes.

INFLUENCE OF pH

The results of this study show that the effect of pH (within the pH range investigated) on extent of corrosion is not in agreement with the generally accepted concepts.

In Fig. 2 instantaneous corrosion rates at the fiftieth day of exposure are plotted against pH. With the exception of water No. 15 (Table 1), all available data are represented in this figure. Fig. 2 shows that there is a general trend of increased corrosion rates with increased pH in the pH range (6.9-8.6). For a given pH value, variations in corrosion rate are, of course, observed; these variations can be explained at least partially by the differences in concentrations of alkalinity (HCO_3^-), dissolved oxygen, calcium, and natural inhibitors such as silicates. Experimental points obtained with low alkalinity waters (below 50 mg per l as $CaCO_3$) are specifically marked in Fig. 2, and it is seen that such waters have a higher corrosion rate than waters with a higher alkalinity.

In discussing the effect of pH (within pH 6-9 - the range of natural waters) upon corrosion, one must consider that hydroxyl ions may exert corrosion stimulating as well as corrosion mitigating influences. With increased hydroxyl ion concentration, the solubility of corrosion products as well as the solubility of $CaCO_3$ decreases. On the basis of this consideration alone, one would assume that corrosion rates decrease with increased pH. It should be considered, on the other hand, that the buffer capacity of a natural water decreases, for a given alkalinity, appreciably with increased pH up to pH 8.4. As will be explained in more detail below, an increase in buffer capacity, associated with a decrease in pH (when considered independent of other factors) should lead to decreased corrosion rates.

The net balance of these opposing effects would define for a given water an optimum pH in which corrosion would be lowest, but the results of this study do not cover a sufficiently broad range of pH values to establish this optimum pH. It can also be expected that different pH-optima are observed for waters of different mineral composition; moreover, the action of many corrosion inhibitors is strongly pH dependent. Detailed laboratory investigations by Larson and Skold (11-14) on the effect of pH on cast iron and steel corrosion in waters having an alkalinity of 125 mg per l (as $CaCO_3$) clearly indicated that the lowest average corrosion rate occurs around pH = 7. The results of Fig. 2, that indicate lower corrosion rates around pH 7 than at higher pH values, are thus in accord with the findings of Larson and Skold for the pH range investigated.

The Solubility of Corrosion Products.—A significant portion of the natural "protective" coatings consists of accumulated products of the corrosion reaction; the insolubility of these corrosion products is an important factor in the formation of protective coatings. The solubility of bivalent iron depends on the pH of the solution. It has been shown experimentally by Baylis (1) and quantitatively evaluated from equilibrium data by Larson and King (15) that its solubility in natural (HCO_3^-, CO_3^{-2} containing) waters in the pH range 6 to 9 is governed by the solubility product of $FeCO_3$ and not (as it is frequently assumed) by the solubility of $Fe(OH)_2$. The concentration of CO_3^{-2} in a natural water, even under neutral or slightly acid conditions, is sufficient to limit the solubility of Fe^{+2} (compare Fig. (2)).

In the pH range of natural waters, soluble bivalent iron consists of Fe^{+2} and $[Fe(OH)]^+$ (16), (22). The solubility of these constituents can be computed by considering (1b) the following equilibria;

$$Fe(OH)_2\ (s) = Fe^{+2} + 2OH^- \qquad K_{S_1} = 8 \times 10^{-16}$$

$$Fe(OH)_2\ (s) = [Fe(OH)]^+ + OH^- \qquad K_{S_2} = 4 \times 10^{-10}$$

$$FeCO_3\ (s) = Fe^{+2} + CO_3^{-2} \qquad K_{S_3} = 2.1 \times 10^{-11}$$

$$FeCO_3\ (s) + OH^- = [Fe(OH)]^+ + CO_3^{-2} \qquad *K = 1.05 \times 10^{-5}$$

$$HCO_3^- = H^+ + CO_3^{-2} \qquad K_2 = 4.6 \times 10^{-11}$$

$$H_2O = H^+ + OH^- \qquad K_W = 10^{-14}$$

in which s equals solid.

The solubility of Fe (II) constituents ($Fe^{+2} + [Fe(OH)]^+$). Moles per liter in natural water can be estimated as a function of the alkalinity (Alk, equivalents per liter) and of the H^+ ion concentration (Moles per liter) by means of the equation.

$$(Fe\ (II)) = \frac{2K_2 + (H^+)}{(Alk)\ (H^+)} \left(K_{S_3} + \frac{{}^*KK_W}{(H^+)} \right) \quad \ldots\ldots\ldots (1)$$

Eq. 1 is valid up to pH = 9 for waters that contain at least 2×10^{-4} equivalents of alkalinity (10 mg per l as $CaCO_3$).

This relationship within the pH range 6-9 is graphically represented in Fig. 3 (b). This figure also gives the solubility of Fe^{+2} governed by the solubility product of $Fe(OH)_2$, that is only of significance in waters that contain no carbonate or at very high pH (above 10). Fig. (b) illustrates that even under neu-

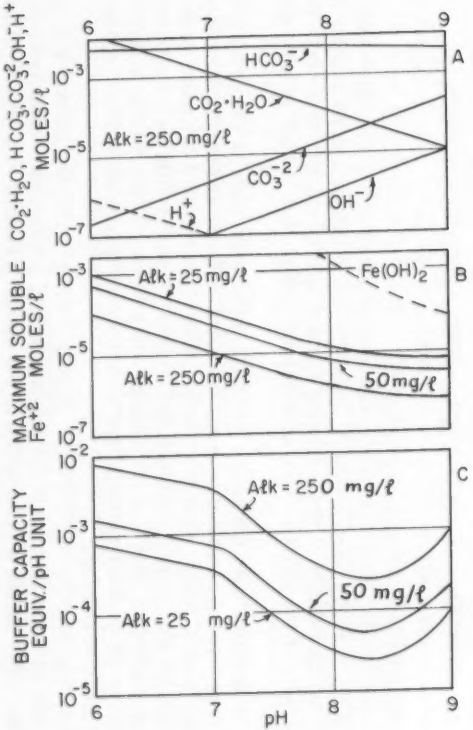

FIG. 3

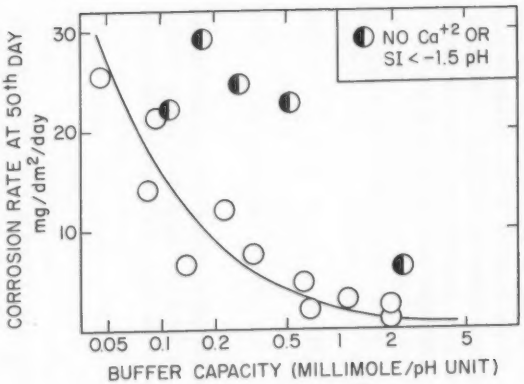

FIG. 4

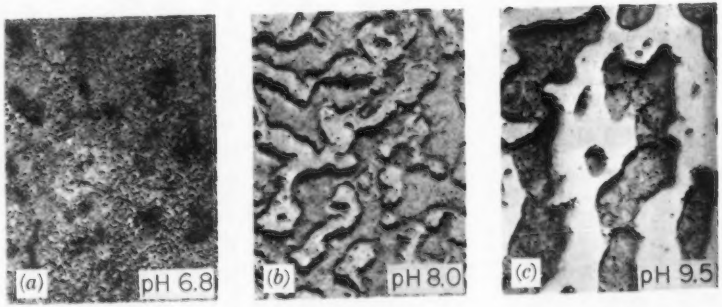

FIG. 5

tral conditions the solubility of $FeCO_3$ is rather small whereas the solubility of Fe $(OH)_2$ in a carbonate-free water would be appreciable. Any bivalent iron is oxidized in oxygenated waters to rather insoluble ferric oxide hydrate at a rate depending primarily on the hydrogen ion concentration.

Corrosion Reactions Influence pH at Iron Surface.—The hydrogen ion concentration in the immediate neighborhood of a corroding iron surface is considerably different from the hydrogen ion concentration in the bulk of the solution (19). Any incipient corrosion will remove hydrogen ions or produce hydroxyl ions in the cathodic reduction of oxygen or hydrogen ions in accordance with

$$O_2 + 4H^+ + 4e = 2H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2a)$$

$$O_2 + 2H_2O + 4e = 4OH \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2b)$$

and

$$2H^+ + 2e = H_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2c)$$

and will, therefore, produce an increase in the pH value of the solution in immediate contact with the cathodic regions of the corroding iron surface. Simultaneously, iron passes into solution in the ferrous conditions at the anodic areas of the corroding metal, such as,

$$Fe + CO_3^{-2} = FeCO_3 + 2e \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3a)$$

$$Fe + HCO_3^- = FeCO_3 + H^+ + 2e \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3b)$$

and

$$Fe + OH^- = Fe(OH)^+ + 2e \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3c)$$

These anodic reactions are possibly followed by a stepwise oxygenation of the bivalent iron constituents into hydrated iron oxide;

$$FeCO_3 + \frac{1}{4}O_2 + \frac{1}{2}H_2O + 2OH^- = Fe(OH)_3 + CO_3^{-2} \quad \ldots\ldots \quad (4a)$$

$$2FeCO_3 + \frac{1}{2}O_2 + 3H_2O + 2OH^- = 2Fe(OH)_3 + 2HCO_3^- \quad \ldots\ldots \quad (4b)$$

or eventually into anhydrous Fe_2O_3.

These anodic reactions precipitate one or more of the alkalinity constituents (CO_3^{-2}, HCO_3^- and/or OH^-). Thus, the pH in the immediate neighborhood of the anodic regions of the corroding surface will be slightly lower than the pH in the bulk of the solution and considerably lower than the pH at the cathodic areas.

It is possible that the acting potential difference (that is the driving force for the corrosion reaction) between the local cathodic and anodic elements increases with a larger difference in pH between cathodic and anodic areas. It can also be reasonably assumed that a heterogeneous film is less protective against corrosion than a more homogeneous coating. Therefore, a large difference in pH between cathodic and anodic areas enhances the heterogeneity of the protective coating.

Buffering constituents (HPO_4^{-2}, $H_2PO_4^-$, HCO_3^-, CO_3^{-2}, acetate and so on) may thus be expected to improve the passivating properties of dissolved oxygen and indirectly cause a retardation of the anodic reaction rate by formation of inhibitive anodic oxide films (4), (17).

Buffer Capacity.—Buffer capacity of a solution is its tendency to resist changes in pH. It may be expressed quantitatively in terms of the amount of strong base or strong acid required to produce a unit change of pH in the solution (23). The lower the buffer capacity of the solution, the greater and more significant will be the changes in the pH values produced by the corrosion reaction near the cathodic and anodic areas of the metal surface. Thus, the actual pH difference between cathode and anode areas is inversely related to the buffer capacity.

The buffer capacity of a natural water depends on its alkalinity and, to even a larger extent, on the pH of the solution. It is then possible to derive the following relation, that interrelates buffer capacity (β in equivalents per pH), alkalinity (in equivalents per liter), and H^+ ion concentration (moles per liter).

$$\beta = 2.3\left[\frac{(H^+)\,(Alk)}{(H^+)+2K_2}\left(\frac{(H^+)}{(H^+)+K_1}+\frac{K_2}{(H^+)+K_2}\right)+(H^+)+(OH^-)\right] \quad \ldots . (5)$$

in which K_1 and K_2 are the first and second acidity constant of $CO_2 . H_2O$ (carbonic acid), respectively ($K_1 = 4 \times 10^{-7}$, $K_2 = 4.6 \times 10^{-11}$).

In Fig. 3(c) buffer capacity, β, is plotted as a function of pH for three different values of alkalinity. This figure illustrates that, for a given alkalinity, buffer capacity decreases with increasing pH up to a pH of 8.4. Beyond pH 8.4, however, the buffer capacity becomes again larger. This buffer capacity relationship may at least partially explain the greater extent of corrosion with increased pH (compare Fig. 2). Considering buffer capacity alone, corrosion rates should become smaller again in waters that are more alkaline than a Ph of 8.4.

It is seen from Fig. 4, in which corrosion rates (at the fiftieth day of exposure) are plotted against the logarithm of buffer capacity, that there is a tendency toward higher corrosion rates in waters with low buffer capacity than in well buffered waters.

Cathode - Anode Area Distribution.—The inspection of specimens that have been immersed in waters of different pH values show remarkable differences in the properties of the coating and the mode of corrosive attack. Fig. 5 gives photographs (21) of the surface condition of specimens that have been exposed for the same time period to waters having the same alkalinity and calcium concentration but different pH values. It is clearly visible that the local anodic and cathodic areas vary remarkably in number and size with different pH values of the solutions; anodic spots become fewer in number and size with different pH values of the solutions and become fewer in number and larger in size the higher the pH of the solution. These findings are in accord with the results of Larson and Skold (12), (13), who report for steel and cast iron an increasing degree of tuberculation as the pH increases.

The effect of pH on Cathode-anode area distribution is not well understood. However, it is reasonable to assume that it may be partly due to the variation of buffer capacity with pH. It is conceivable that under conditions of large pH differences between the local cathodic and anodic elements (small buffer capacity) these elements have a tendency to agglomerate and to grow in area.

Colloidal Migration.—Furthermore, colloid chemical aspects must be considered. In neutral or slightly acid solutions, the ferric oxide colloids are positively charged and have a tendency to migrate electrophoretically toward cathodic areas. In this case, iron oxide will tend to be distributed rather uniformly over

the corroding surface (see Fig. 5(a)), and the dimensions of the respective anodes and cathodes remain small. Anodic pores and small cathodic spots can be clogged more efficiently than large anodic or cathodic areas by cathodic or anodic inhibitors or a combination of both. In alkaline solutions, however, these iron oxide colloids are negatively charged. Furthermore, the rate of oxygenation of ferrous to ferric compounds increases with increasing pH. The anodic corrosion products will thus be oxidized as rapidly as they are formed, and the negatively charged ferric oxide colloids are precipitated at the anodic areas and thus concentrate at the sites of the initial corrosion. This hydrated ferric oxide does not restrain the anode reaction significantly. Corrosion products continue to diffuse slowly through the oxide and are precipitated after oxygenation in the immediate neighborhood of the anodes. In the case of alkaline solutions, hydrous ferric oxide is laid down unevenly and leads to the formation of separate anodic and cathodic areas. Oxygen has less access to the neighboring (originally cathodic) sites that become progressively covered with ferric oxide. Differential aeration cells are set up with the shielded parts of the cathodes tending to become anodic. Such a sequence allows progressive growth of anodic areas and, eventually, to pitting and the formation of tubercles.

The Catalytic Properties of OH-Ions.—Bonhoeffer and Heusler (2), (7) and earlier Kabanov and Leikis (9), presented theoretical and experimental evidence that hydroxyl ions (besides their influence on the solubility of corrosion products and $CaCO_3$ and on the buffer capacity) strongly catalyze the anodic iron dissolution in oxygen free solutions. But if one assumes that the cathodic electrode process in oxygen containing waters is rate determining, such a concept would be of no practical importance for fresh water corrosion. As already mentioned, initial corrosion is mainly under cathodic control, but in the later stages of corrosion, the rate of the anodic reactions codetermines to a marked extent the overall corrosion rate. It appears possible, therefore, that hydroxyl ions, as catalysts of the anodic dissolution reaction, may exert a corrosion accelerating influence.

ALKALINITY AND OXYGEN

It is a well known fact that corrosion rates are usually lower in waters with high alkalinity (high in bicarbonate content) than they are in waters with low alkalinity. The ideas presented may serve as a partial explanation of such experience. An increased alkalinity content enhances the buffer capacity and restrains the solubility of Fe^{+2} and Ca^{+2}. Coatings formed in waters with very low alkalinity are not very protective against corrosion even if their hydrogen ion concentration is in the generally favorable pH region of 7 (See waters No. 10, 13).

Since bicarbonate and carbonate ions are readily hydrated and, therefore, not specifically adsorbed at the metal surface, their inhibitive action must be indirect. Similar inhibitory effects, as those of bicarbonate, are observed with other buffering ions, such as acetate, HPO_4^{-2}, $H_2PO_4^{-}$. It has been demonstrated experimentally (4), (17) that such buffering ions are better inhibitors in the presence of dissolved oxygen than in oxygen free solutions. Prior and Cohen (17) have shown that corrosion eventually becomes greater in deaerated than in aerated HPO_4^{-2} containing solutions. The view has therefore been put forward that dissolved oxygen is mainly responsible for the ability of buffering ions to inhibit the corrosion of iron (3), (4), (17).

Thus, dissolved oxygen has a dual influence on the corrosion process. First, it is a good cathodic depolarizer, increasing the rate of the cathodic process and, when the latter is the controlling factor, the rate of corrosion. In the initial phase of corrosion, the corrosion rate is much higher in aerated waters than the rate of oxygen free water. Secondly, dissolved oxygen increased the electrode potential. It has been shown (4) that an oxidizing agent is frequently necessary for the formation of a protective anodic film. High concentrations of dissolved oxygen thus lower the probability of corrosion by improving the anodic films. It is considered that dissolved oxygen is adsorbed on the surface of the iron and takes part in the formation of a protective film.

Anodic Films.—There are varying theories concerning the nature of the passive anodic film, but it is well established that such films consist mainly of anhydrous γ-Fe_2O_3. These films are very thin (50-200 A°) and chemically inert. Most of the hydrated ferric oxide is located in rather thick inclusion that protrude above the oxide film (17). The general mechanism of formation of passive films of γ-Fe_2O_3 is not very well understood, but it is postulated that γ-Fe_2O_3 is formed stepwise over the oxidation of magnetite $(Fe_3O_4 \times H_2O)$. According to Feitknecht (5), magnetite can be formed topochemically over Fe^{+II}, Fe^{+III} -hydroxal salts by means of very slow oxygenation of ferrous iron in buffered solutions. The further oxidation of magnetite to anhydrous γ-Fe_2O_3 also occurs topochemically. Bicarbonate ions through pH control enhance the passivation of anodes by dissolved oxygen. Their effect results from their contribution to the buffer capacity of the solution at the metal surface. The formation of passive anodic films results in partial anodic control of the electrochemical action.

Cathodic or Anodic Control?—Many authors have emphasized that corrosion in aerated water is usually under cathodic control, that is, the anode reaction rate is more rapid than the rate of the cathodic oxygen reduction, and since both reactions must proceed at the same rate, the cathodic reaction is rate determining. Such a conclusion, however, is generally based on corrosion experiments of short duration and is thus valid only for the initial phases of corrosion. Much evidence, however, substantiates the theory that the anodic reaction rate codetermines the corrosion rate in the later stage of corrosion especially after films have deposited on the anode area. Measurements of the corrosion potential as a function of time frequently show, especially in well buffered waters, an increase of the electrode potential (21). Such ennoblement of the corrosion potential indicates a decrease in anode area, a retardation of the anode reaction rate, or a combination of these. With increased time of exposure of iron to water, anodic control of the corrosion rate may become progressively more evident, especially in bicarbonate waters at a pH of 7.

In fresh water corrosion, therefore, anodic inhibitive effects, as well as accelerating effects (such as chloride) must be considered too.

A dense anodic film layer affects the anodic process by reducing the "free" effective area of the anodic surface. It may act (1) by hindering the diffusion of the anodic products into the solution or (2) by creating conditions at the interface that (a) decelerate the electron transfer or (b) inhibit chemical reactions (for example the hydration of Fe^{+2} ions).

It is well known that passive γ-Fe_2O_3 is destroyed by chloride and to a smaller extent by sulfate (24). These ions are anodic corrosion stimulants and increase the anodic area. Potential versus time data show that addition of chloride decreases the electrode potential, thus indicating increase of the free anode

area fraction. Chloride and buffer capacity are thus anodic antagonists. Larson (12-14), realizing this antagonistic behavior, has determined the corrosive-inhibitive relationship for various equivalent ratios of chloride-bicarbonate for given pH values.

The ultimate corrosion in aerated natural waters after very prolonged periods of immersion (that is, years) is presumably to a large extent under anodic control. A steady state of continuous break down and repair of the passive anodic film determines the ultimate corrosion rate. If dissolved oxygen becomes nearly exhausted, under stagnant conditions, as for example in dead end pipes, the γ-Fe_2O_3 film breaks down, the corrosion process then comes under cathodic control, and corrosion rates increase.

CALCIUM CARBONATE

Calcium carbonate is an important component of the protective coatings that are formed in many water supply pipes. The saturation index ($SI = pH - pH_S$, in which pH_S is the pH at hypothetical saturation with respect to Ca^{+2} and alkalinity) has been used frequently to measure the tendency of a water to deposit

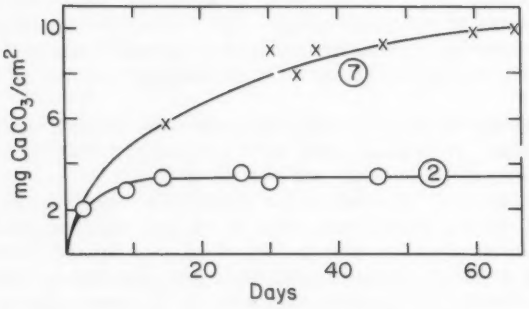

FIG. 6

$CaCO_3$. Fig. 6 shows the amount of $CaCO_3$ deposited within 50 days as a function of the saturation index for all the tests in which an analysis of the coatings has been made. It is evident from this figure that the amount of $CaCO_3$ deposited cannot be predicted by the saturation index. The pH of the solution immediately adjacent to the cathodic areas is higher than in the bulk of the solution. Thus, the deposition of $CaCO_3$ is primarily controlled by the electrochemical changes at the metal surface, that is, it is influenced by the rate of the corrosion reaction and depends also on the buffer capacity of the solution and on the flow rate. The data in Fig. 6 (b) illustrate that there is no simple correlation between the amount of $CaCO_3$ deposited in the film and the protective effect of the coating against corrosion.

In Fig. 7, $CaCO_3$ deposition is plotted against time for two representative examples (20). It is remarkable that the harder water (water No. 2) that is slightly oversaturated with $CaCO_3$ deposits less $CaCO_3$ than the softer water

(water No. 7) that has a negative saturation index. In the soft water, that has a relatively small buffer capacity, the corrosion reaction produces a more significant increase in the pH value and a more pronounced shift in the $CaCO_3$ equilibrium near the metal surface that was the case with the harder water, with a higher buffer capacity (18). The corrosion results (see Fig. 1) clearly show that the $CaCO_3$ deposited from the hard and buffered water is more effective in retarding corrosion than the $CaCO_3$ precipitated from the soft and less buffered water. From the results in Fig. 7, it can be seen that after a relatively short time of exposure, no more $CaCO_3$ is deposited from the oversaturated water and $CaCO_3$ is not dissolved by the slightly aggressive water. We must assume that the corrosion products cling together with the deposited $CaCO_3$. The physical character of the coating is altered with time of exposure. $CaCO_3$ is "cemented" to the pipe wall and shielded by corrosion products. The slightly oversaturated water finds no further crystallization nuclei to continue the deposition, and the slightly aggressive water cannot dissolve $CaCO_3$ that has been deposited, incidentally, due to the electrochemical corrosion reaction. The

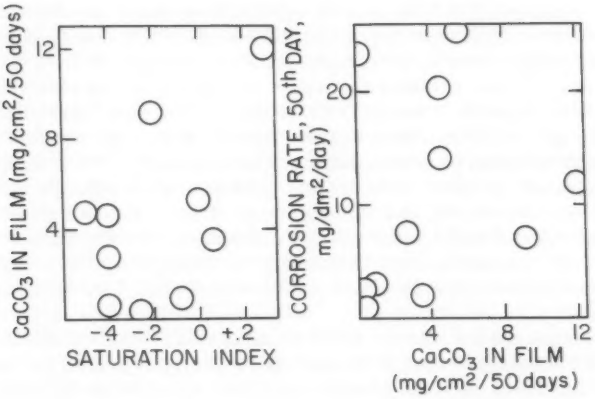

FIG. 7

author has shown previously (19) that $CaCO_3$ is not uniformly distributed within the film. The relative amount is highest in the layers closest to the iron surface.

Although neither the $CaCO_3$ saturation equilibrium (SI) nor the relative amount of $CaCO_3$ deposited at the electrode surface are significant parameters of corrosion inhibition, the results (Table 1) nevertheless illustrate that the presence of calcium ions in the water is beneficial in reducing the extent of corrosion. Fig. 3 shows that waters that contain no Ca^{+2} are, for a given buffer capacity, more corrosive. It appears that $CaCO_3$ acts only under certain favorable conditions as a valuable corrosion inhibitor.

Mechanism of Inhibition by Calcium Carbonate.—The inhibitive action of a coating is associated with the extent of the effective coverage of the metal surface. Such coatings may be regarded as heterogeneous films composed of

cathodic and anodic areas. $CaCO_3$ is primarily deposited within the cathodic areas. Such a deposition may very well decelerate the penetration of oxygen molecules through the film to the iron surface. It should be realized, however, that cathodic films consist mainly of hydrated iron oxide and have a porous structure and, thus, a generally high degree of permeability for molecules. Oxygen, for example, permeates membranes (polyethylene, cellophane, and so on) rather easily. The results obtained in this investigation (Fig. 6) fail to indicate that $CaCO_3$ enhances the diffusion barrier of the cathodic film to a significant extent.

The author has shown in an earlier paper (21) that deposited $CaCO_3$ acts preferentially by reducing the area of the anodes of the corrosion cell. This is based on the observation that rapid reduction of corrosion rates in calcium bearing waters is always accompanied by an increase (ennoblement) of the corrosion potential. Shifts of the corrosion potential arise primarily from alterations in the relative sizes of the cathode and anode areas. In the systems investigated, the cathode area is generally much larger than the anode area. Here the reduction of anodic areas affects the anode area fraction (anodic area per total area) significantly whereas the cathode area fraction is altered only slightly. A protective coating, if it acts merely by blocking more anodic than cathodic sites, reduces the anode area more than it reduces the cathode area, leading to a shift of the compromise (corrosion) potential in the positive (noble) direction (8). Conversely, if the calcium carbonate deposited at the electrode surface would retard the cathodic reaction to a larger extent than the anodic reaction, the mitigation of corrosion due to $CaCO_3$ deposition would then, contrary to experimental observation, be accompanied by a decrease in the corrosion potential. The decrease in anode area fraction, as it occurs through $CaCO_3$ deposition, leads simultaneously to an ennoblement of the corrosion potential and to a reduction of the corrosion current (21). Although the deposits of $CaCO_3$ on the cathodes are substantially greater than the deposits on the anodes, the latter are far more effective in increasing polarization and, therefore, in inhibiting corrosion.

Different explanations can be given to account for the effect of deposited $CaCO_3$ on the reduction of anodic film areas. A partially protective film formed over the cathodes sets up a differential aeration cell with the shielded cathodes tending to become more anodic than the original anodes. This results in continuous changes in the locations of anodes and cathodes on the metal. The $CaCO_3$ that was originally deposited at the cathodic areas may, thus, eventually become part of the anodic coating in which the corrosion products shield it from being attacked by hydrogen ions. It may also be assumed that $CaCO_3$ is not only deposited on the cathodic areas but also on the neighboring sites, that is within the boundaries of the cathode and anode areas, thus decreasing progressively the anodic areas. Another possible cause for an anodic deposition of $CaCO_3$ suggests an exchange of Ca^{+2} ions with $FeCO_3$ formed at the anodes (15) according to the reaction

$$FeCO_3 + Ca^{+2} = CaCO_3 + Fe^{+2} \quad \ldots\ldots\ldots (6)$$

The equilibrium constant of this reaction $\left(K = (Fe^{+}2)/(Ca^{+2}\right)$ is about 4×10^{-3}). This reaction may proceed to some extent from left to right if the calcium ion concentration is larger than the Fe^{+2} concentration.

$CaCO_3$ should be classified as "primarily anodic" inhibitor since it reduces the anode area and decelerates the anodic reaction. It is thus understandable

that the protective effect of the coating does not depend on the bulk quantity of deposited $CaCO_3$. Only the amount of $CaCO_3$ that acts on the anodes is of high significance for the protective properties. The results of this study show that relatively small amounts of deposited $CaCO_3$ caused a pronounced mitigation of corrosion in waters in the pH range 7 to 7.4 (waters No. 1, 3, 5) whereas large amounts of precipitated $CaCO_3$ failed to render the coating very protective in waters of higher pH (8.2 to 8.6) (waters No. 9, 11, 12, 14). The area of large anodic spots is reduced less efficiently than the area of small anodic pores by the deposition of $CaCO_3$. Thus, the extent of corrosion in the alkaline waters (pH 8.2 to 8.6) in which anodic areas are large (compare Fig. 5) was more pronounced than in waters with lower pH values. On the other hand, $CaCO_3$ precipitated from solutions with pH 7 to 7.4, was capable of clogging the small anodic pore areas and, therefore, decreasing the anodic area fraction by a sufficient amount to render the coating protective. Although the saturation indices were of similar magnitude (-0.5 to +0.3 pH units) in both group of experiments, the more inhibitive waters around a pH of 7 were higher in calcium content than the more corrosive waters at higher pH. Thus, the findings indicate that calcium ions in the presence of alkalinity, regardless of saturation index effectively enhance the protective effect of the coating against corrosion. In experiments 10 and 13, the pH was favorable for a protective coating, but insufficient amounts of $CaCO_3$ were deposited because of a strongly negative saturation index.

The results show that $CaCO_3$ acts as a valuable corrosion inhibitor if capable of blocking or reducing the size of the local anodic sites of a corroding iron surface. Conditions for clogging anodic sites are more favorable at a pH around 7 than at higher pH values, or if the water contains high concentrations of calcium ions.

Low alkalinity waters are saturated with $CaCO_3$ at high pH-values only, but corrosion control through the action of deposited $CaCO_3$ is not very effective at high pH. Thus, waters of low alkalinity are frequently very corrosive even if they have been treated with lime to attain $CaCO_3$ saturation. Conversely, waters with a high alkalinity and calcium concentration are $CaCO_3$-saturated at lower pH values (around pH = 7). Such waters are capable of forming very protective coatings.

Inhibition by deposited $CaCO_3$ is somewhat similar in principle, but entirely different in mechanism, to the inhibition by metaphosphate. Metaphosphate is primarily a cathodic inhibitor, although most metaphosphate is deposited at anodic sites (10). The inhibitive action of metaphosphate is better in slightly acid or neutral solutions than in alkaline waters (6). The influence of pH on the cathode-anode area distribution may account for this effect. The small cathodic spots at a lower pH can be clogged more efficiently by phosphate than the large cathodic areas that prevail in the alkaline pH-region.

PRACTICAL ASPECTS

The ideas presented are based on a limited number of results obtained under specific test conditions and are, thus, not necessarily immediately applicable to practice. However, the tentative conclusions reached may be of value in partly explaining the relative basic corrosivity of various qualities of water, and the proposed "working hypotheses" may lead to further, more systematic investigations that will be of practical significance. Many questions remain

unanswered. The problem of designing water treatment for corrosion control can only be solved if the mutual interaction of corrosion stimulating and retarding factors is adequately understood.

Flow Rate.—All results in this study were obtained from experiments with a very low flow velocity. The variation of flow rate certainly changes the corrosivity of the water, however, the variable should still show the same general trends of influence. Increased flow rates accentuate the corrosive behavior of the waters. It has been shown (13) that increasing flow velocity provides increasing protection with low proportions of corrosion stimulating factors to inhibitive factors. On the other hand, the degree of protection decreases with increasing velocities as this proportion increases. At higher flow velocities, more oxygen, but also more inhibitors, are supplied to the iron surface. The supply of dissolved oxygen to the cathodes is, however, limited by the rate of penetration through the cathodic film. With increased flow rates more buffering constituents (CO_2, HCO_3^-, CO_3^{-3}) are also supplied to the iron surface per unit time, thus creating conditions equivalent to a higher buffer capacity.

Water Treatment for Corrosion Control.—The addition of lime and soda ash increases alkalinity (if no precipitation occurs) and reduces the solubility of corrosion products and $CaCO_3$. This would certainly lead to a reduction of the corrosive attack if it were not accompanied by an increase in pH, that affects the cathode-anode area distribution unfavorably and causes, in most cases, a decrease in buffer capacity. The net balance of the favorable and unfavorable aspects of the addition of alkalinity components varies with waters of different alkalinity content. In waters of low alkalinity (that is, below 50 mg per l as $CaCO_3$), the addition of $Ca(OH)_2$ or $NaCO_3$ leads to a large percentual increase in alkalinity (and Ca^{+2}) whereas the buffer capacity is not changed appreciably. The beneficial influence of increase in alkalinity (and in the case of lime addition in Ca^{+2} concentration) is, however, partly compensated by the influence of the pH-change on the buffer capacity. In such low alkalinity waters, the solubility of ferrous iron and of $CaCO_3$ is high. This large decrease of the solubility of these constituents by both an increase in alkalinity and pH compensates or even outweights the otherwise unfavorable aspects of a high pH (such as, the cathode-anode area distribution). It is interesting to note that Baylis (1), who found a decrease in the extent of corrosion upon addition of lime, made his investigations with Baltimore, Maryland water (Bellemonte Reservoir) having an alkalinity of approximately 25 mg per l. Whitman, Russell, and Altieri (25) reported no change in corrosion rates with an increase in alkalinity and pH up to pH-9.5, on the basis of investigations made with Cambridge, Massachusetts tap water that has an alkalinity of 47 mg per l.

In waters of higher alkalinity content, the addition of alkalinity components generally leads to increased corrosion rates. With such waters, the solubility of the constituents of the coatings ($CaCO_3$, $FeCO_3$) is already relatively small at a pH of 7. Dosage with lime or soda ash causes only a small percentual increase in alkalinity (and calcium content), whereas a raise in pH value causes a marked decrease of buffer capacity.

"Red Water".—A very great proportion of the corrosion products becomes included in the coating formed at the iron surface, and only a very small fraction of the corroded material remains suspended, presumably as colloidal ferric oxide, in the water. The occurrence of red water cannot be correlated with the extent of corrosion in the distribution system. At low pH, at which the oxygenation of ferrous constituents is slow, less iron oxide will be retained in the coating than under alkaline conditions, under which ferrous constituents are

rapidly oxidized. At a high pH value, calcium ions aid in coagulating the negatively charged ferric oxide colloids. It can be further inferred that, in the presence of greater amounts of electrolytes, colloidal iron oxide is more rapidly precipitated at the iron surface because electrolytes partly neutralize the charge and compact the diffuse double layer of the colloidal particles.

Table 2 shows some experimental results with waters of different pH on the relation between the proportion of the amount of iron lost in corrosion and the amount of iron deposited in the coating. The results clearly indicate that with high pH a greater fraction of iron oxide is retained in the coating. Although addition of lime, Na_2CO_3 or combinations of the two may, under certain conditions, lead to higher corrosion rates, such treatment may prevent the occurrence of "red water" and may "hide" corrosion. It is questionable whether this is, from a practical point of view, as relevant as a decreased carrying capacity of the pipe caused by corrosion and precipitation. (These considerations do not apply to iron bearing well waters.)

Unexplained Behavior of One Water.—The corrosivity of water No. 15 cannot be explained on the basis of the variables presented herein. This illustrates how much care must be exercised in predicting the corrosive behavior of a water

TABLE 2.—pH INFLUENCES RETENTION OF IRON OXIDE IN THE COATING

pH (1)	Alkalinity and Hardness, in mg per l as $CaCO_3$ (2)	Fe in coating per weight loss (3)
8.40	205	0.94
7.65	205	0.92
7.35	205	0.71
6.95	205	0.58
6.55	205	0.50
8.40	117	0.77
6.40	117	0.44

from its mineral content. This water has an unusual high nitrate content (37 mg NO_3^- per l). In addition, slime deposits and growth of iron bacteria occurred in this experiment. It is reasonable to assume that these two factors account for the very corrosive behavior of this particular water.

Natural waters may contain minor constituents (organic substances, silicates, and so on) that, even if present in trace quantities, frequently have inhibitive (occasionally also insiduous accelerating) properties. Such factors must not be overlooked.

It is evident that we are not yet able to correlate reliably the chemical composition of a water with its corrosiveness to iron. More experimental and theoretical work relating to the fundamentals involved is needed. Water works practice should place more emphasis on the experimental determination of the corrosion characteristics of the water. The treatment of a water for corrosive control should be designed on the basis of reliable experimental evaluation rather than on generalized and simplified theoretical concepts.

CONCLUSIONS

As a result of the research described in this paper, the following conclusions may be drawn:

1. In the early phases of corrosion in aerated waters the electrode process is under cathodic control. After prolonged periods of exposure, the anodic reaction rate codetermines to a marked extent the overall corrosion rate.

2. Extent of corrosion is higher the lower the buffer capacity. In waters of high buffer capacity more homogeneous and more protective coatings are formed than in waters of low buffer capacity. Buffering constituents (CO_3^{-2}, HCO_3^-) enhance the passivating properties of dissolved oxygen and thus indirectly retard the anodic reaction rate by formation of strongly inhibitive anodic oxide films.

3. There is a general trend of increased corrosion rates with increased pH in the pH range 6.9 to 8.6. Variations of corrosion rates with pH can, at least partly, be explained by the change in buffer capacity associated with a change in hydrogen ion concentration. Furthermore, pH has a marked effect on the cathode-anode area distribution. The size of the local anodes increases with increased pH.

4. Deposited $CaCO_3$ reduces the anode area fraction. Conditions for clogging anodic pores are more favorable at a pH of 7 than at higher pH values.

ACKNOWLEDGMENT

The author gratefully acknowledges the valuable suggestions and the critical advice given by Thurston E. Larson of the Illinois State Water Survey.

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Journal of the
SANITARY ENGINEERING DIVISION
Proceedings of the American Society of Civil Engineers

TRITIUM AS A GROUND WATER TRACER

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SYNOPSIS

Tritium in the form of tritiated water is a nearly perfect ground water tracer. Its only serious disadvantage is derived from its radioactive properties and the potential effects on public health of extremely small concentrations of radioisotopes. The potential biological risks of using tritium in large scale water tracing operations are treated and compared with the possible benefits.

INTRODUCTION

The ability to balel and subsequently identify water, even after a movement of several miles through the earth, is of considerable interest to the sanitary engineer and others concerned with water resource protection or development. Perhaps most typical of tracer applications is the relatively simple situation involving the origin of contamination in a well water and whether a nearby leaching field was the origin. On a larger scale, there is often need for de tailed information on the the rate and direction of ground water movement in order to evaluate the ultimate capacity of a ground water resource. Typical of situations requiring knowledge of ground water flow are the sewage reclama of situations requiring knowledge of ground water flow are the sewage reclamation operations now under development in the Los Angeles area. Questions relating to the maximum possible rate of pollution travel, who is benefiting from the recharge operation, and how much water is ultimately recovered can

Note.—Discussion open until April 1, 1961. To extend the closing date one month, a written request must be filed with the Executive Secretary, ASCE. This paper is part of the copyrighted Journal of the Sanitary Engineering Division, Proceedings of the American Society of Civil Engineers, Vol. 86, No. SA 6, November, 1960.

[1] W. J. Kaufman, Assoc. Prof., San. Engr., Univ. of Calif., Berkeley, Calif.

be more correctly and economically answered with the aid of tracers. One of the most potentially interesting applications of water tracers is for geological exploration of deep formations of the earth in connection with injection dis-- posal of radioactive and other toxic wastes.

There are numerous substances that will serve satisfactorily as water tracers, but only under a certain set of circumstances. In setting forth the desirable characteristics of the ideal or perfect tracer, it immediately becomes apparent that very few, if any, materials are entirely satisfactory. What are the criteria of the ideal ground water tracer? Obviously, it must move in exactly the same manner as the water that it is expected to trace without in any way modifying the transmission properties of the aquifer. Moreover, it must obviously be detectable. A most important criterion is low adsorptive loss to the porous medium, a condition that immediately eliminates all cations, including both the normal chemical forms and those available as radioisotopes. The chloride ion and other members of the halogen group, such as iodine, are adsorbed relatively little and have been used successfully in many instances. For example, iodine-131, accompanied by stable iodine as a carrier, has found application in the secondary recovery of petroleum. The organic dyes, particularly sodium fluorescein, have been widely used as water tracers, but have been repeatedly demonstrated to be unreliable where the test formation contained humus or other organic material. For qualitative answers fluorescein will continue to serve usefully in ground water tracing.

As a general rule, small concentrations of water miscible substances are likely to be retained, at least to some degree, by adsorption on soil colloids. For this reason a majority of the radionuclides, unless "carried" by large concentrations of a stable isotope, are unsuitable as water tracers. It is apparent that the most likely tracer of water is water itself. Ordinary water contains three isotopes of hydrogen; hydrogen-2 or deuterium and hydrogen-3 or tritium, and of course the most common, hydrogen of mass number one. In addition, there are three naturally occurring isotopes of oxygen as well as several artificially created radioisotopes. These isotopes, when a part of the water molecule, will move through most natural media without significant adsorptive loss. From the standpoint of faithfully tracing water, they would appear to be ideal.

In addition to the adsorption criterion, a tracer should be measureable at a reasonable cost in low concentrations. It should cause no impairment of any beneficial use of the labeled water, and should undergo no physical or chemical change that would either hinder its measurement or result in its loss from the water mass. The cost of the tracer, together with the cost of measurement, is often an important factor, particularly where a study may require several hundred analyses and entail the labeling of hundreds of millions of gallons of water. It is generally preferable that the tracer be nearly absent from the water to be labeled, although there are instances in which this is not necessary; the investigator merely relies on concentration differences to distinguish between the two waters.

The tracer that appears to meet these many requirements most completely is the hydrogen isotope tritium. Tritium is to be preferred over the other components of water, such as deuterium or the oxygen isotopes, primarily on

the basis of either the cost of the isotope or its measurement at the desired level of sensitivity.

NATURE AND OCCURRENCE OF TRITIUM

Tritium is the only radioisotope of hydrogen. It has a mass number of 3 and decays by pure beta emission with a half-life of 12.5 yr. Tritium occurs naturally, being produced at a constant rate in the earth's atmosphere as a result of cosmic ray interaction with nitrogen atoms. Libby[2,3] has reported the average natural world-wide tritium content of land rainfall as 3.3 tritium atoms per 10^{18} hydrogen atoms, a radio-activity concentration equal to 10^{-8} microcurie (μc) per cubic centimeter. A microcurie is the amount of radioactive material undergoing 2,200,000 disintegrations per minute. Occasionally Libby observed precipitation with a natural tritium content exceeding 2×10^{-7} μc/ml.

In the spring of 1954, the entire hydrologic distribution of the world's tritium was suddenly altered by the Castle series of thermonuclear weapons tested in the Pacific. As a result of this test series, the concentration of tritium in precipitation in North America rose from about 10^{-8} μc/ml to more than 8×10^{-6} μc/ml, a nearly one thousand fold increase. By mid-1955, the tritium content of precipitation in the Northern Hemisphere had decreased to 10^{-7} μc/ml, approximately ten times the pre-weapons test figure. In 1956, tritium concentrations rose a second time and in the past two years have been fluctuating between ten and one hundred times the natural value of 10^{-8} μc/ml; these fluctuations are presumably due to the continued testing of thermonuclear weapons and to variations in transport and deposition of tritium from the upper atmosphere. Measurements made in the spring of 1959, both in Europe and the United States, indicated rainfall concentrations of tritium were again exceeding the 3×10^{-6} μc/ml level.

The Castle series of weapons tests introduced into the atmosphere, and subsequently into the earth's surface and ground waters, an enormous quantity of tritium labeled water. Several investigators, including Begemann and Libby[4], have measured the concentration of this tracer in precipitation and surface and ground waters, and have arrived at general conclusions regarding the gross movement of water in the atmosphere and on earth. Studies of movement of bomb produced tritium through an aquifer in New Mexico have been reported by von Buttlar[5]. The New Mexico study suggests that a "post-Castle" tritium content of precipitation may provide, without cost to the investigator, a useful hydrologic tool. In certain instances this may prove to be the case. However, the occurrence and movement of tritium in ground and surface waters

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2 "Research to Assay Rain and Surface Water for Natural Tritium Content," by W. F. Libby, Final Report, Air Force Contract A.F. 18, 600-564, Univ. of Chicago, June 1, 1954.

3 "The Natural Distribution of Tritium," by Kaufman, Sheldon and W. F. Libby, Physical Review, 93, 6, pp. 1337-1344, March 15, 1954.

4 "Continental Water Balance, Ground Water Inventory and Storage Times, Surface Ocean Mixing Rates and World-Wide Water Circulations Patterns from Cosmic-Ray and Bomb Tritium," by Begemann, Friedrich and W. F. Libby, Geochemica et Cosmochimica Acta, 12, 4, pp. 277-296, 1947.

5 "Investigating Ground Water by Analysis of Atmospheric Tritium," by Har von Buttlar, Journal A. W. W. A., 50, 11, pp. 1533-1538, November, 1958.

has been so greatly confused by subsequent weapons tests that it is doubtful whether it will prove of significant value.

MEASUREMENT OF TRITIUM

Tritium is a low energy beta emitter, the maximum energy being only 0.018 mev and the average energy 0.0059 mev. For this reason, and because the tritium content of a sample cannot be raised by ordinary concentration techniques, tritium measurement represents a rather difficult problem. Two measurement methods are available. Tritium, in the form of tritiated water, may be converted into the molecular form of hydrogen gas and introduced into one of the conventional types of gas-filled detectors, such as a Geiger or proportional counter. Under these conditions, the disadvantages of the low decay energy are largely eliminated, and the measurement made with nearly 100% efficiency.

A second and more recently developed method of tritium measurement uses the liquid scintillation counter. With this equipment, a tritiated water sample is dissolved in a transparent solvent containing a phosphor and placed in a glass vial. The low energy beta radiation (of low penetrating power) interacts with the phosphor to produce small pulses of light that readily pass through the solvent-water mixture and the glass container. The sample is viewed by two photo-multiplier tubes, often referred to as photoelectric cells, that convert the light to electrical pulses. The electrical pulses are passed through electronic circuitry to a scaler or recorder. Although the liquid scintillation counter is complex and costly, the sample preparation and counting procedure are quite simple and require little technician time or experience in execution.

The sensitivities of the gas counting and liquid scintillation counting systems are essentially comparable and will permit the detection of tritium concentrations as low as 5×10^{-7} $\mu c/ml$ with a counting period of 30 minutes[6]. Unfortunately, this "sensitivity" is not adquate to detect natural tritium levels or even to measure with precision those resulting from weapons testing. This inadequacy may be overcome by electrolysing a liter or more of water, a process that reduces the volume of the sample, but also increases greatly the tritium concentration of the remaining water. The electrolysis-gas counting methodology is currently being used by several groups in the United States. A measurement by this technique requires several weeks to complete and is estimated to cost on the order of 200 dollars.

The application of natural tritium obviously has several serious disadvantages. As noted above, its measurement is time-consuming and costly. Furthermore, as considered in the previous section, the investigator has no control over its occurrence that has become increasingly complex with the continued testing of thermonuclear weapons.

PUBLIC HEALTH IMPLICATIONS OF USING RADIOACTIVE TRACERS

The precise extent of biological damage to humans from exposure to low-levels of ionizing radiations is yet uncertain. However, it is generally agreed that all radiation exposure, even that of natural background, is probably harmful to man and his descendants. An increasing mass of experimental data lends

6 "Low-Level Tritium Measurement with the Liquid Scintillation Spectrometer," by R. M. Hours and W. J. Kaufman, Paper No. 51, Nuclear Engineering and Science Conference, April, 1960.

support to the often expressed philosophy that all radiation exposure is harmful, and hence, all unnecessary exposure to radiation should be avoided. Unfortunately, an equally convincing mass of data leads to the conclusion that any operation involving radioactive materials must necessarily result in some release of these materials to the biosphere. Thus, the engineer-physicist group concerned with developing the material benefits of nuclear science is brought into sharp conflict with the physician-biologist group concerned primarily with the protection of individual and public health. The public, at best only partially informed, may be expected to view radiation effects on a personal basis and consequently support the position of the biologist. How may this apparent impasse be resolved to the mutual safety and benefit of all concerned? The only answer would appear to be the equating of material benefits of nuclear science to the costs measured in terms of undesirable biological effects. Furthermore, it is essential that "costs," or individual "risks" be measured in the same framework as other risks of everyday life, that is, the risks of driving, smoking, over-eating, breathing polluted atmospheres, and perhaps even crossing the street.

Prior to 1934, the acceptable occupational exposure level to radiation was 100 rem per yr. The occupational level has been progressively reduced and at present rests at 5 rem per yr, as recommended by the International Commission on Radiological Protection in April, 1956. (The rem is the quantity of any ionizing radiation such that the energy imparted to a biological system per gram of living matter has the same biological effect as that from x-radiation giving an absorbed dose of 100 ergs per gram.) The reductions represent compromises between zero and the capabilities of technology both to use and to control radiation. It is significant that at none of these levels has there ever been demonstrated damage to the individual. The International Commission now recommends that the whole population dose up to age 30 not exceed 10 rem considering all sources of radiation exposure except natural background. Subtracting from this value, exposures resulting from medical usage of radiation and fallout, a dose of 4 to 5 rem for 30 yr, remains that might be looked upon as a "bank" from which withdrawals may be made (providing they are invested in enterprises bringing real and significant benefits to the affected population).

An examination of the most recent recommendations of the United States National Committee on Radiation Protection and Measurements (N.C.R.P.) has been published by L. S. Taylor[7]. This Committee, on which there are representatives from the (AMA), the U. S. Public Health Service, and other public and private agencies, has recommended that the radiation or radioactive material outside a controlled area, but attributable to normal operations in that area, shall be such that it is improbable that any individual will receive a radiation dose of more than 0.5 rem in any one year. This value is 10% of the occupational limit for whole body or gonadal exposure. Similarly, the National Committee has recommended that concentrations of radioisotopes in air and water outside a controlled area should not exceed one-tenth of the maximum permissible concentrations for occupational exposure. In each case, the concentrations may be averaged over a period of one year. It should be noted that the National Committee's value of 0.5 rem per year for 30 yr amounts to 15 rem, exceeding by a factor of three the International Commission's exposure bank of 4 to 5 rem. This is not an inconsistency, since 0.5

[7] "Maximum Permissible Radiation Exposures to Man," by L. S. Taylor, Health Physics, 1, 2, pp. 200-204, September, 1958.

rem per yr is the individual maximum that is most likely to be reached for any large group of people, whereas, the 4 to 5 rem value is the average exposure for an entire population group.

The deliberations leading to the previously cited recommendations were largely concerned with genetic damage, it having been assumed that a threshold radiation dose existed below which somatic damage did not occur. There is, however, convincing evidence, from studies of animal populations, that whole body radiation exposures ranging from 100 to 1200 roentgens result in shortening of life-span in direct linear proportion to the absorbed dose. This relationship has been shown to exist for laboratory animals with both acute and chronic exposures. If the linear relationship of radiation dose to effect can be properly applied by exprapolation to very low doses, the implications are of great interest to the sanitary engineer. Jones[8] concludes that small-animal data suggest that one roentgen of radiation exposure is equivalent to 5 to 15 days of physiologic aging, that is, life-span shortening. He further indicates this relation to be valid for doses of a few roentgens or less. As might be expected, all biophysicists do not concur with the low-dose, proportional-effect concept, pointing to evidence suggesting that small radiation doses may stimulate physiologic mechanisms that appear to extend the average life-span, perhaps by affording the animal additional protection against disease. It is evident from the literature that a great deal of additional research will be necessary to demonstrate conclusively the validity of the proportional effect concept at low radiation dosages. It is improbable that this will ever be accomplished on an ipidemiological basis. However, existing experimental evidence and scientific opinion favoring the proportional concept will most certainly influence public health policy in establishing standards not regulating radiation exposure of the population. It would thus appear that we are likely to pursue a conservative investment policy in making withdrawals from our exposure "bank", and it is quite likely that many public health workers will even find it most difficult to accept the bank philosophy.

In the previous paragraph, somatic effects expressed as life-span shortening of the presently living population were considered. To realize the entire consequence of radiation exposure, a brief analysis of the genetic effects of radiation is in order. The best current estimates of the genetic effect of radiation place the mammalian mutation-doubling dose at about 50 r with most estimates ranging from 30 to 80 r.[9] Since natural background ranges from 4 to 5 r, it is apparent that only about 10% of the normal human mutation rate is due to radiation and that the "bank" suggested by the International Commission, if fully and continuously used for the development of nuclear technology, would ultimately result in approximately a 10% increase in the human burden of mutant genes. What is the cost of this additional burden? From the National Academy of Science report it can be computed that in-

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[8] "The Nature of Radioactive Fallout and its Effects on Man," by H. B. Jones, Hearing before the Special Subcommittee on Radiation, Eighty-Fifth Congress, Washington, 1957, pp. 1100-1137.

[9] "The Biological Effects of Atomic Radiation," National Academy of Sciences, Summary Report, 1956.

creasing human radiation exposure by 5 r per generation would result, after perhaps 40 generations, in 0.2% of live births having tangible genetic defects.

MAXIMUM PERMISSIBLE CONCENTRATIONS OF TRITIUM IN WATER

Tritium, introduced into the human body in the form of tritiated water, is very quickly dispersed in the body fluids. Pinson and Langham[10] have measured the period of equilibration of ingested tritiated water with body fluids to be from 2 to 2.5 hr. If no further intake of tritium occurs, a period of approximately 12 days is necessary for one-half of the tritium burden to be excreted from the body. This period is termed the "biological half-life." Since the radioactive half-life is considerably greater (12.5 yr), the biological half-life essentially equals the effective half-life that determines the rate of loss of a radionuclide from an organ.

The 1957 U.S. Atomic Energy Commission regulations for protection against radiation[11] place the Maximum Permissible Concentration of tritium in water at 0.016 μc/ml, this value applying to the general population in the vicinity of a controlled area. (The Maximum Permissible Concentration (M.P.C.) of tritium in water for continuous occupational exposure, stated elsewhere[12] (June 5, 1959), is 0.03 μc/cc. One tenth of this value may be regarded as maximum permissible in the neighborhood of a controlled area or nuclear installation.) Using the more recent recommendations of the National Committee on Radiation Protection of 0.5 rem per year and other information on the biological effects of tritium radiation, a maximum, permissible concentration of 0.003 μc/ml may be computed. If an individual consumed water containing this concentration of tritium for several weeks, the tritium body-burden would approach 120 μc and the whole body exposure rate would reach the permissible limit of 0.010 rem per week or 0.5 rem per year. In the case of short duration or intermittant exposure, it is permissible to compute the exposure rate on a yearly average basis. It is worthy to note that the computation of radiation exposures to the whole body or gonads from tritium is probably one of the most reliable of all the internal dose computations.

SELECTING A TRITIUM CONCENTRATION FOR WATER TRACING

Let us assume that we are to trace a body of ground water that serves as a source of supply for a community of several hundred thousand persons, and that tritium is the tracer under consideration. What concentration should be used, or in fact should we permit any tritium radioactivity to be employed? On the basis of the U.S. Atomic Energy Commission (AEC) regulations, derived from the recommendations of the National Committee on Radiation Protection, we could presumably use some fraction of the Maximum Permissible Concentration for the population at large. Since the duration of the investigation would perhaps be not more than a few years, no individual would be exposed for more than a fraction of a lifetime. Thus, considering the

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10 Journal of Applied Physiology, by E. A. Pinson and W. H. Langham, 10, 1, pp. 108-126, January, 1957.

11 "Standards for Protection Against Radiation," Federal Register, Title 10, Chapter 1, Part 20, January 29, 1957.

12 Nat. Bur. of Standards Handbook, 69, June 5, 1959.

official M.P.C., the relatively short duration of exposure, the sensitivity of our measuring equipment, and the cost of tritium, we might arrive at a tracer concentration of about 50% of the lifetime M.P.C. The AEC has, in fact, granted a license for the use of this concentration for tracing a domestic water supply.

Let us examine the project in terms of the material benefits likely to accrue and objectively compare these benefits to the biological risks of the investigation. For this comparison it is convenient to take an actual proposed investigation that is now under consideration.

The Los Angeles County Flood Control District has for some years followed a practice of replenishing the ground water at some sixteen locations in the county by artificially introducing surplus water. In such operations, the earth serves as both a storage reservoir and distribution system for the communities and industries utilizing the affected aquifers. The spreading basin located at the mouth of the San Gabriel Canyon is typical of such installations. Water is a costly and essential commodity in the life and economy of the San Gabriel Valley and the coastal regions of Los Angeles county. In purchasing water and discharging it into the earth, several questions are immediately raised. The most important of these is what fraction of the water is actually recovered for beneficial use. Another question of some importance in financing an expanded replenishment program is who are the beneficients and to what extent are various pumpers receiving the spread waters. Partial answers to these questions can, of course, be obtained by an examination of pumping records, ground water levels, and similar hydrologic data. However, it appears that only by labeling the recharged water can reliable quantitative data be obtained. What are these answers worth in dollars? This is a most difficult question, and the answer can only be arrived at in an indirect manner. The combined ultimate water use of the Main San Gabriel Basin and the East Central Coastal Basin is estimated to be 445,000 acre ft annually. Placing the value of water at $30 per acre ft, the annual water "bill" will amount ultimately to nearly 15 million dollars. With only local water available to meet this demand, an annual over-fraft of 163,000 acre ft is predicted. This demand can, to a large measure, be feasibly met by replenishment operations. Such operations would make ground water recharge a 3 million dollar a year public enterprise. Knowledge enabling the efficient operation of the replenishment system could, over a 20-yr period, conceivably benefit the population to the extent of several millions of dollars.

It has been proposed to introduce tritium into a flow of 40 cfs such that the tritium concentration amounts to 1.6×10^{-4} μc/ml. This water would be introduced into spreading basins at the mouth of the San Gabriel Canyon and would ultimately find its way into the main San Gabriel Basin and perhaps even through the Whittier Narrows to the Coastal Basin. Under the conditions of the test, the tracer would be added continuously for 35 days, labeling a total of 825 million gal of water and requiring 500 curies of tritium. Samples would then be taken from various wells serving the major municipalities of the region and the movement of the traced water mass followed to the limits of measurement sensitivity. It is quite possible that the traced water would be detected through the Main Basin and perhaps even to the Pacific Ocean. It should be noted that the tritium detection limit of 5×10^{-7} μc/ml noted earlier will enable the detection of the labeled water even after a 300-fold dilution.

What are the potential biological risks of such an investigation? In estimating these risks it is, of course, essential to anticipate the worst possible conditions that could develop. However, the assumptions made in estimating the effects of the worst condition should be plausible and guided by established scientific principles. Where a reasonable doubt exists we should use the conservative assumption in the interests of erring on the side of safety. Let us consider two possible situations involving the exposure of individuals and populations.

1. Assume that the entire 825 million gal remains in the locale of the spreading basin and serves a small group of individuals throughout their entire lives. This is a highly improbable assumption considering the mobility of ground water. It is examined solely to illustrate the maximum possible effects on a single individual. The ingestion of 1.6×10^{-4} μc/ml would cause an exposure over a period of 70 yr of 1.9 rem. Adopting the proportional effect philosophy and using Jones' value of 10 days of life-span shortening per roentgen (or 6 days per rem), the statistical life-span reduction would be about 11 days.

A more probable maximum individual effect would be reached by assuming a more reasonable, yet conservative, exposure period; 1 yr for example, at the full concentration of 1.6×10^{-4} μc/ml. The effect on life-span would be reduced by 1/70 or to about 4 hr.

2. Assume that the entire 825 million gal are used by only domestic consumers of the Main and Coastal Basins over a period of several years. Here we are obliged to make three additional assumptions, a daily per capita water consumption of 150 gal, a reuse factor of 2, the latter resulting from a natural and artificial recharge of municipal sewage, and a fractional water use by domestic consumers of 0.5. If it is assumed that the period of use is small in comparison to the physical half-life of tritium, we may omit the reduction in effect due to radioactive decay. The total population dose may then be computed as, (total individual dose) x (total number of persons exposed), or total population dose = 126 (tracer used, in curies) x (fraction of water used by domestic consumers) x (reuse factor) ÷ (per capita water use in gal per day)

$$= \frac{126 \times 500 \times 0.5 \times 2}{150} = 420 \text{ rem - pop.}$$

(The rem is related to the radiation adsorbed dose (rad) by the relative biological effectiveness of the radiation. In the case of tritium, this quantity is 1.7 and hence: rem = 1.7 x rad.) The value 420 rem-pop. is independent of any dilution of the tracer, of the number of persons consuming the traced water, and of the period of consumption. Again assuming a shortening of life-span of 6 days per rem, a total life-span cost to the present generation of consumers of 2,500 man days results. This would appear to be an excessively large value, but spread over a population of 100,000, it would amount to an individual cost of only 0.6 hr.

It is of interest to take a specific disease and compute its particular contribution to the total life-span shortening effect. Lewis[13] has estimated the population mortality rate of radiation induced leukemia to be 0.2 per 100,000 per yr for each roentgen of radiation exposure. Muller[14] has computed that one absorbed roentgen of whole-body radiation would cause

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13 "Leukemia and Ionizing Radiations," by E. B. Lewis, Science, 125, pp. 965-972, May 17, 1957.

14 H. J. Muller, p. 1067, Reference 7.

about 6 cases of leukemia per 100,000 exposed individuals. In the case of the proposed Los Angeles County investigation, there could result 250 man-

$$\text{rad} \times \frac{6 \text{ leukemia cases per rad}}{100{,}000 \text{ persons}}$$ or 0.017 cases of leukemia. Since the incidence of leukemia is approximately 5 cases per 100,000 per year, it is obvious that the occurrence of 0.017 cases during and subsequent to the test period would hardly significant and certainly not statistically distinguishable as a deviation from the normal rate.

To what extent will the proposed test increase the genetic burden of the exposed population? Assuming 50% of the population in the Main and Coastal basins are of age 30 or less, the population exposure of genetic significance would be 250/2 or 125 rad-population. From the Natural Academy of Sciences Report[15] it may be estimated that the 125 roentgen-pop. would introduce 0.4 mutants. Assuming an average normal population burden of 5 mutant genes, the 0.4 mutants spread over a population of 50,000 persons would only increase the mutant burden by 0.00017%.

How do the biologic effects of the proposed study compare with the effects of common environmental factors that modify health or cause early death? Jones[16] has computed the life shortening effects associated with the normal characteristics and habits of man. These effects are expressed as years loss of life-span. Several typical values are as follows:

City versus country dwelling	-5 yr
Smoking 1 package of cigarettes per day	-9 yr
25% overweight	-3.6 yr
Accidental death to an individual in U.S.A.	-2.3 yr
Pedestrian motor-vehicle accidents for an individual living in an urban area	-0.4 yr
Motor-vehicle accidents involving driver and passengers	-0.67 yr

In comparison with the preceding figures, the 2,500 man-days lost per assumed 100,000 persons affected (or 0.00007 yr per individual) would certainly appear to be of little significance. What are the total consequences of the 0.4 undesirable mutant genes introduced into the population? It has been estimated that the present mutant burden of the human race results in a life-span shortening of as much as 10 yr. If we assume the mutant burden to be 5 genes, one gene contributes, on the average, 2 yr of life-span shortening to any individual carrying it. If we further assume an elimination rate of the induced mutant of 5% per generation and a static population, it can be shown that the 0.4 genes might possibly cause a total life-span shortening in the next 40 generations of 0.4 x 2 x 20 = 16 years of 5900 man-days. It might be stated that the cost in genetic life-span shortening per living individual to his descendants is bout 0.0017 yr.

The total biological expenditure, both somatic and genetic, might be in the order of 2,500 + 5,900 or 8,400 man-days, whereas the potential material benefits of the investigative venture might well range over one million dollars.

The argument is often presented that most risks of living, such as those cited in the preceding list, are incurred voluntarily by each individual, whereas

15 "The Biological Effects of Atomic Radiation," Nat. Acad. of Sci., Summary Report, 1956, p. 27.

16 "Estimation of Effect of Radiation Upon Human Health and Life Span," by H. B. Jones, Proceedings of the Health Physics Society, pp. 114-126, June, 1956.

introducing radioactivity into the environment exposes all persons to the risk of biological damage without the individual's consent. To a degree this is certainly a valid contention. However, it is difficult to imagine how one could "voluntarily" avoid being a pedestrian or, in a city such as Los Angeles, avoid being an automobile passenger.

CONCLUSIONS

Tritium, in the chemical form of tritiated water, is a nearly ideal water tracer and perhaps the only satisfactory means of tracing water great distance through the earth. The methods available for measuring tritium are sufficiently sensitive to permit the use of concentrations only 1% of the Maximum Permissible Concentration cited in U. S. AEC regulations. However, the belief that physiologic aging and the incidence of leukemia are increased in direct linear proportion to even very small radiation doses, raises serious doubt regarding the propriety of tritium as a tracer in which human consumption of the traced water occurs. It is believed that the use of tritium is justified if it can be demonstrated that the material benefits of its use are commensurate to the total biological risks to the affected population. The case of a proposed tracer study in Los Angeles County is cited as a situation in which the use of tritium would be justified.

In recent years ionizing radiation has been singled out among the host of stresses endured by the human race and given exhaustive scrutiny. This emphasis on the effects of radiation, though certainly not to be belittled, is a two-edged sword. It has alerted the public health worker to the hazards of radiation, but it has also made it nearly impossible to consider radiation hazards in the same framework as the innumerable other hazards to longevity that we encounter each day of life. We are unable to equate objectively biologic risk and material benefit, yet we must. It is a simple fact that the human race must pay a price in biologic damage if it is to realize any significant benefit from nuclear science. The sanitary engineer can play an important role in radiation control, providing he realistically appraises benefit and risk and can convince the public his equation is a valid and acceptable one.

Journal of the
SANITARY ENGINEERING DIVISION
Proceedings of the American Society of Civil Engineers

DERIVATION OF FLOW EQUATIONS FOR SEWAGE SLUDGES

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SYNOPSIS

This paper has been prepared to bring together the solution of equations which have been derived by others and reported in various texts, journal articles, and theses. The extent of coverage is limited to time-independent non-Newtonian liquids flowing in capillary and rotational viscometers and smooth pipes.

INTRODUCTION

Flow equations for sewage sludges have been presented[2] in detail together with interpretation of their use. Since the solution of these equations is found in a number of books, theses, and journal articles, it was felt that some merit would attach to the recording of them in paper. The form of the arrangement follows generally that of the previous paper, and therefore no attempt is made to repeat the interpretive material.

This paper is concerned only with time-independent non-Newtonians. In particular, the paper commences with a discussion of shear stress-shear rate relationships for various types of non-Newtonians. Based on these relationships, flow equations applicable to the capillary viscometer and rotational viscometer are then derived. The paper concludes with the development of the pressure

Note.—Discussion open until April 1, 1961. To extend the closing date one month, a written request must be filed with the Executive Secretary, ASCE. This paper is part of the copyrighted Journal of the Sanitary Engineering Division, Proceedings of the American Society of Civil Engineers, Vol. 86, No. SA 6, November, 1960.

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[2] "Flow Equations For Sewage Sludges," by Vaughn C. Behn, Journal Water Pollution Control Federation, Vol. 32, July, 1960, p. 728.

drop, Reynolds Number, and friction factor relationships for smooth pipes carrying non-Newtonians.

In general, the solutions presented represent the work of others. The paper is referenced for those who prefer to search the original authors.

Notation.—The letter symbols adopted for use in this paper are defined and arranged alphabetically for convenience of reference in Appendix V.

SHEAR STRESS-SHEAR RATE RELATIONSHIPS

General Relationships.—The shear stress-shear rate relationships for various classes of fluids are given as:

Newtonian

$$\tau = \mu \frac{du}{dy} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Non-Newtonians

Bingham Plastic

$$\tau - \tau_y = \eta \frac{du}{dy} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Pseudoplastic

$$\tau = K \left(\frac{du}{dy}\right)^n \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Any time independent fluid

$$\tau = F \left(\frac{du}{dy}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

or

$$\frac{du}{dy} = G(\tau) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

Relationships in Round Pipe or Capillary.—The shear stress-shear rate relationships in a pipe or capillary take the form:

Newtonian

$$\tau = \mu \left(-\frac{dv}{dr}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

Non-Newtonian

Bingham Plastic

$$\tau - \tau_y = \eta \left(-\frac{dv}{dr}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

Pseudoplastic

$$\tau = K \left(-\frac{dv}{dr}\right)^n \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

Any time independent fluid

$$\left(-\frac{dv}{dr}\right) = G(\tau) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

Relationships in a Rotational Viscometer.—In a rotational viscometer the shear stress-shear rate relationships take the form

Newtonian

$$\tau = \mu R \left(\frac{d\omega}{dR}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

Non-Newtonian

Bingham Plastic

$$\tau = \tau_y + \eta\, R\left(\frac{d\omega}{dR}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

Pseudoplastic

$$\tau = K\left(R\frac{d\omega}{dR}\right)^n \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (12)$$

Any time independent fluid

$$R\left(\frac{d\omega}{dR}\right) = G(\tau) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (13)$$

The use of the relationship $\frac{dv_r}{dR}$ for shear rate in this set of equations is equally permissible since

$$\frac{dv_r}{dR} = R\,\frac{d\omega}{dR} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (14)$$

Apparent Viscosity.—The terms apparent viscosity, μ_a, is sometimes found convenient. By definition

$$\mu_a = \frac{\tau}{\left(\frac{du}{dy}\right)} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (15)$$

From this definition, the following equations are seen to define the apparent viscosity for different fluids.

Newtonian

$$\mu_a = \mu \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (16)$$

Non-Newtonian

Bingham Plastic

$$\mu_a = \frac{\tau_y}{\left(\frac{du}{dy}\right)} + \eta \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (17)$$

Pseudoplastic

$$\mu_a = K\left(\frac{du}{dy}\right)^{n-1} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (18)$$

Any time independent fluid

$$\mu_a = \frac{F\left(\frac{du}{dy}\right)}{\frac{du}{dy}} \text{ or } \frac{\tau}{\left(\frac{du}{dy}\right)} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (19)$$

LAMINAR FLOW EQUATIONS FOR A CAPILLARY VISCOMETER

General.—In this section there are developed flow equations for various types of fluids in capillaries or round tubes, Laminar flow is assumed.

Newtonian.—For a Newtonian flowing in a round pipe or capillary, the shear stress-shear rate relationship may be altered to

$$dv = -\frac{\tau\, dr}{\mu} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (20)$$

Assuming that τ increases linearly from zero at the center line to τ_w at the wall, an expression for τ at any distance r from the centerline is (see Appendix I)

$$\tau = \frac{r}{r_w} \tau_w \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (21)$$

Substituting this value of τ,

$$dv = \frac{-r \tau_w}{\mu r_w} dr \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (22)$$

Integrating from the center line to the wall yields

$$\int_{v_c}^{v_w} dv = -\int_{r_c}^{r_w} \frac{\tau_w r}{\mu r_w} dr \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (23)$$

Assuming that $v_w = r_c = 0$, the solution becomes

$$v_c = \frac{\tau_w D}{4 \mu} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (24)$$

Now the total volumetric flow, Q, is given by

$$Q = \frac{\pi D^2 V}{4} = +\int_{r_c}^{r_w} 2 \pi r v \, dr = -\int_{v_c}^{v_w} \frac{2 \pi r \mu v \, dv}{\tau} \quad \ldots\ldots\ldots\ldots (25)$$

Therefore,

$$\frac{\pi D^2 V}{4} = \int_0^{\frac{\tau_w D}{4 \mu}} \frac{r_w 2 \pi \mu v \, dv}{\tau_w} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (26)$$

Which reduces to $\frac{8 V}{D} = \frac{\tau_w}{\mu}$.

This equation is merely an altered form of the Hagen-Poiseuille equation. The advantage of this form is that $\frac{8 V}{D}$ is seen by inspection to be the shear rate at the wall.

Bingham Plastic.—The flow characteristics of a Bingham Plastic differ from that of a Newtonian in that a yield stress must be reached before any shear rate exists. The shear stress varies linearly from τ_y to τ_w. Since $\frac{dv}{dr}$ is zero to the radial distance r_y where the shear stress τ_y is reached, the assumption is made that at the center of the tube a plug of diameter 2 r_y moves along as a solid mass. Outside the plug there is a linear relationship between shear rate and shear stress. In this portion of the tube

$$dv = -\frac{1}{\eta} \left(\tau - \tau_y \right) dr \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (27)$$

Assuming that for r greater than r_y and τ greater than τ_y

$$\tau = \frac{r}{r_w} \tau_w \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (28)$$

Then

$$dv = -\frac{1}{\eta} \left(\frac{r}{r_w} \tau_w - \tau_y \right) dr \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (29)$$

Integrating in the region between the outer edge of the plug and the wall,

$$\int_{v_i}^{v_w} dv = -\frac{1}{\eta}\int_{r_i}^{r_w}\left(\frac{r}{r_w}\tau_w - \tau_y\right) dr \qquad \begin{matrix} r_i \geq r_y \\ v_i \geq v_y \end{matrix} \quad \ldots\ldots\ldots\ldots \quad (30)$$

Assuming $v_w = 0$, this integration reduces to

$$v_i = \frac{1}{\eta}\left(\frac{r_w \tau_w}{2} - \frac{r_i^2 \tau_w}{2 r_w} - \tau_y r_w + \tau_y r_i\right) \ldots\ldots\ldots\ldots \quad (31)$$

At the outer edge of the plug, $v = v_y$ and $r = r_y$

$$v_y = \frac{1}{\eta}\left(\frac{r_w \tau_w}{2} - \frac{r_y^2 \tau_w}{2 r_w} - \tau_y r_w + \tau_y r_y\right) \ldots\ldots\ldots\ldots \quad (32)$$

The actual flow in the plug is equal to q_1 where

$$q_1 = \pi r_y^2 v_y = \frac{2\pi}{\eta}\left(\frac{r_y^2 r_w \tau_w}{4} + \frac{\tau_y r_y^3}{4} - \frac{\tau_y r_y^2 r_w}{2}\right) \ldots\ldots \quad (33)$$

The flow in the space not occupied by the plug is given as q_2 and may be computed from

$$q_2 = \int_{r_y}^{r_w} 2\pi r_i \, dr_i \, v_i \ldots\ldots\ldots\ldots\ldots\ldots \quad (34)$$

Substituting the previously derived value of v

$$q_2 = \frac{2\pi}{\eta}\int_{r_y}^{r_w}\left[\frac{r_w \tau_w r_i}{2} - \frac{r_i^3 \tau_w}{2 r_w} - \tau_y r_w r_i + \tau_y r_i^2\right] dr_i \ldots \quad (35)$$

Which upon integration yields

$$q_2 = \frac{2\pi}{\eta}\left[\frac{r_w^3 \tau_w}{4} - \frac{r_w r_y^2 \tau_w}{4} - \frac{r_w^4 \tau_w}{8 r_w} + \frac{r_y^4 \tau_w}{8 r_w} - \frac{\tau_y r_w^3}{2} + \frac{\tau_y r_y^2 r_w}{2} + \frac{\tau_y r_w^3}{3} - \frac{\tau_y r_y^3}{3}\right] \ldots\ldots\ldots\ldots \quad (36)$$

The total flow in the tube or capillary is given by Q where

$$Q = q_1 + q_2 = \frac{2\pi}{\eta}\left[\frac{r_w^3 \tau_w}{8} + \frac{r_y^4 \tau_w}{8 r_w} - \frac{\tau_y r_w^3}{6} - \frac{\tau_y r_y^3}{12}\right] \ldots\ldots \quad (37)$$

The following relationships are now introduced

$$Q = \pi r_w^2 V, \quad \tau = \frac{r}{r_w}\tau_w, \quad 2 r_w = D \ldots\ldots\ldots\ldots\ldots \quad (38)$$

The final resulting equation is

$$\frac{8V}{D} = \frac{\tau_w}{\eta}\left[1 - \frac{4}{3}\frac{\tau_y}{\tau_w} + \frac{1}{3}\left(\frac{\tau_y}{\tau_w}\right)^4\right] \ldots\ldots\ldots\ldots \quad (39)$$

This well known equation, first derived by Buckingham, was first derived in the sanitary engineering literature by H. E. Babbitt and D. H. Caldwell.[3,4,5] G. E. Alves gives an interesting solution of this equation.[6,7] Note that the equation reduces to the Newtonian as a special case.

The shear rate at the wall may now be found for a Bingham Plastic since by definition

$$\tau_w - \tau_y = \eta \left(-\frac{dv}{dr}\right)_w \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (40)$$

or

$$\left(-\frac{dv}{dr}\right)_w = \frac{\tau_w}{\eta} - \frac{\tau_y}{\eta} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (41)$$

Substituting the value of τ_w derived from the Buckingham equation

$$\left(-\frac{dv}{dr}\right)_w = \frac{8\,V}{D}\left(\frac{1}{\left[1 - \frac{4}{3}\frac{\tau_y}{\tau_w} + \frac{1}{3}\left(\frac{\tau_y}{\tau_w}\right)^4\right]}\right) - \frac{\tau_y}{\eta} \quad \ldots\ldots\ldots\ldots \quad (42)$$

Pseudoplastic.—The pseudoplastic fluids can frequently be represented by a power function relationship between shear stress and shear rate. When this is so

$$\left(-\frac{dv}{dr}\right)^n = \frac{\tau}{K} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (43)$$

Once again the assumption is made that $\tau = \frac{r}{r_w}\,\tau_w$.

Therefore

$$\left(-\frac{dv}{dr}\right)^n = \frac{r}{K}\frac{\tau_w}{r_w} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (44)$$

This expression is solved for dv and the result integrated from a point r_i from the center line to a point on the wall. The velocity varies from v_i to 0.

$$-\int_{v_i}^{0} dv = \left(\frac{\tau_w}{r_w K}\right)^{\frac{1}{n}} \int_{r_i}^{r_w} \frac{1}{r^n}\,dr \quad \ldots\ldots\ldots\ldots\ldots \quad (45)$$

Integration of this expression yields

$$v_i = \frac{\left(\frac{\tau_w}{K}\right)^{\frac{1}{n}} r_w}{(1 + 1/n)}\left[1 - \left(\frac{r_i}{r_w}\right)^{(1+1/n)}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (46)$$

Now

$$Q = V\frac{\pi D^2}{4} = \int_0^{r_w} 2\,\pi\, r_i\, v_i\, dr_i \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (47)$$

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[3] "Laminar Flow of Sludges in Pipes with Special Reference to Sewage Sludge," by H. E. Babbit and D. H. Caldwell, Univ. of Illinois Bulletin, Vol. 37, No. 12, Nov. 14, 1939.

[4] "Turbulent Flow of Sludges in Pipes," by H. E. Babbitt and D. H. Caldwell, Univ. of Illinois Bulletin, Vol. 38, No. 13, Nov. 19, 1940.

[5] See also by same authors Transactions, Amer. Inst. of Chemical Engrs., Vol. 37, 1941, p. 237.

[6] "Non-Newtonian Flow," by G. E. Alves, A chapter in "Fluid and Particle Mechanics," Ed. by C. E. Lapple, Univ. of Delaware, Newark, Del., 1951.

[7] "Pipe Line Design for Non-Newtonians," by G. E. Alves, D. F. Boucher, and R. L. Pigford, Chemical Engrg. Progress, Vol. 48, No. 8, 1952, pp. 385-393.

So

$$V\frac{\pi D^2}{4} = \frac{2\pi}{(n+1)}\left(\frac{\tau_w}{K}\right)^{\frac{1}{n}}(n\, r_w)\int_0^{r_w}\left[1-\left(\frac{r_i}{r_w}\right)^{\left(1+\frac{1}{n}\right)}\right]dr_i \quad \ldots\ldots \quad (48)$$

Recalling that $D = 2\, r_w$, this expression may be simplified to

$$V = \frac{2\, n\, r_w}{(6n+2)}\left(\frac{\tau_w}{K}\right)^{\frac{1}{n}} \quad \ldots\ldots \quad (49)$$

or

$$\tau_w = K\left(\frac{8\, V}{D}\right)^n\left(\frac{3\, n+1}{4n}\right)^n \quad \ldots\ldots \quad (50)$$

This is the flow equation for a power function non-Newtonian. A. B. Metzner derives a different form of this same equation.[8] This equation reduces to the Newtonian form for the special case $n = 1$ and $K = \mu$.

Once again it is possible to derive the shear stress at the wall from the basic definition of the shear stress-shear rate relationship.

$$\left(-\frac{dv}{dr}\right)_w = \left(\frac{\tau_w}{K}\right)^{\frac{1}{n}} \quad \ldots\ldots \quad (51)$$

Substituting the expression for τ_w just derived,

$$\left(-\frac{dv}{dr}\right)_w = \frac{8\, V}{D}\left(\frac{3\, n+1}{4\, n}\right) \quad \ldots\ldots \quad (52)$$

Any-Time-Independent Non-Newtonian.—The previous solutions have depended upon the shear stress-shear rate relationship. A solution is possible without defining this relationship and the result is general for all time-independent non-Newtonians.

A general expression for any fluid in a pipe or capillary is

$$\mu_a = \frac{\tau}{\left(-\frac{dv}{dr}\right)} \quad \ldots\ldots \quad (53)$$

Therefore,

$$-dv = \frac{\tau}{\mu_a}\, dr \quad \ldots\ldots \quad (54)$$

Integrating this expression from some point r_i from the centerline to the wall

$$\int_{v_i}^{0} -dv = \int_{r_i}^{r_w}\frac{\tau}{\mu_a}\, dr \quad \ldots\ldots \quad (55)$$

Introducing the expression $\tau = \frac{r}{r_w}\,\tau_w$.

$$v_i = \frac{\tau_w}{r_w}\int_{r_i}^{r_w}\frac{r\, dr}{\mu_a} \quad \ldots\ldots \quad (56)$$

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[8] "Non-Newtonian Technology," A chapter by A. B. Metzner in "Advances in Chemical Engineering," Ed. by T. B. Drew and J. W. Hoopes, Academic Press, Inc., N. Y., 1956.

This expression can not now be integrated directly since μ_a is not known as a function of r. However, it is still rigorously permissible to write an expression for Q.

$$Q = \int_0^{r_w} 2\pi r_i v_i \, dr_i \quad \ldots\ldots\ldots\ldots\ldots (57)$$

Which becomes

$$Q = \frac{2\pi\tau_w}{r_w} \int_0^{r_w} \left[\int_{r_i}^{r_w} \frac{r\,dr}{\mu_a} \right] r_i \, dr_i \quad \ldots\ldots\ldots (58)$$

The definite integral on the right hand side of Eq. 58 is simplified by using integration by parts.

$$\int_0^{r_w} \left[\int_{r_i}^{r_w} \frac{r\,dr}{\mu_a} \right] r_i \, dr_i = \left[\frac{r_i^2}{2} \int_{r_i}^{r_w} \frac{r\,dr}{\mu_a} \right]_0^{r_w} - \int_0^{r_w} \frac{r^3\,dr}{2} \quad \ldots\ldots (59)$$

or

$$\int_0^{r_w} \left[\int_{r_i}^{r_w} \frac{r\,dr}{\mu_a} \right] r_i \, dr_i = \int_0^{r_w} \frac{r^3\,dr}{\mu_a} - \int_0^{r_w} \frac{r^3\,dr}{2\mu_a} = \frac{1}{2} \int_0^{r_w} \frac{r^3\,dr}{\mu_a} \quad \ldots\ldots (60)$$

Therefore Q may be written

$$Q = \frac{\pi\tau_w}{r_w} \int_0^{r_w} \frac{r^3\,dr}{\mu_a} \quad \ldots\ldots\ldots\ldots\ldots (61)$$

It is now convenient to change the independent variable from r to τ, remembering that

$$r = \frac{r_w \tau}{\tau_w} \quad \text{or} \quad dr = \frac{r_w}{\tau_w} d\tau \quad \ldots\ldots\ldots\ldots (62)$$

Therefore

$$Q = \frac{\pi r_w^3}{\tau_w^3} \int_0^{\tau_w} \frac{\tau^3\,d\tau}{\mu_a} \quad \ldots\ldots\ldots\ldots\ldots (63)$$

Now introduce the quantity x where

$$x = \frac{Q}{\pi r_w^3} \quad \ldots\ldots\ldots\ldots\ldots\ldots (64)$$

So that

$$x\,\tau_w^3 = \int_0^{\tau_w} \frac{\tau^3\,d\tau}{\mu_a} \quad \ldots\ldots\ldots\ldots\ldots (65)$$

Differentiating

$$\frac{dx}{d\tau_w}\,\tau_w^3 + 3\,\tau_w^2\,x = \frac{\tau_w^3}{\mu_a} \quad \ldots\ldots\ldots\ldots (66)$$

But $Q = V\pi r_w^2$ and $x = \dfrac{Q}{\pi r_w^3} = \dfrac{V}{r_w} = \dfrac{2V}{D}$

Thus

$$\frac{d\left(\frac{2V}{D}\right)}{d\,\tau_w}\,\tau_w + 3\left(\frac{2V}{D}\right) = \left(\frac{\tau_w}{\mu_a}\right)_w \quad \ldots\ldots\ldots\ldots (67)$$

Now $\left(\frac{\tau_w}{\mu_a}\right)_w$ is immediately recognized as the shear rate at the wall, $\left(-\frac{dv}{dr}\right)_w$.

Therefore

$$\left(-\frac{dv}{dr}\right)_w = \frac{3}{4}\left(\frac{8V}{D}\right) + \frac{1}{4}\,\frac{d\left(\frac{8V}{D}\right)}{d\tau_w}\,\tau_w \quad \ldots\ldots\ldots\ldots\ldots \quad (68)$$

This expression is known as the Rabinowitsh-Mooney equation, the solution here being that given by M. Mooney who also demonstrates how a slippage factor may be incorporated.[9] The equation is also derived by B. B. Bird, et al.[10]

Metzner and J. C. Reed have demonstrated the following useful alteration of this equation.[11]

Since

$$\frac{d\left(\frac{8V}{D}\right)}{\frac{8V}{D}} = d\left(\ln\frac{8V}{D}\right) \quad \ldots\ldots\ldots\ldots\ldots \quad (69)$$

and

$$\frac{d(\tau_w)}{\tau_w} = d(\ln\tau_w) \quad \ldots\ldots\ldots\ldots\ldots \quad (70)$$

$$\left(-\frac{dv}{dr}\right)_w = \frac{3}{4}\left(\frac{8V}{D}\right) + \frac{1}{4}\left(\frac{8V}{D}\right)\frac{d\left(\ln\frac{8V}{D}\right)}{d(\ln\tau_w)} \quad \ldots\ldots\ldots\ldots\ldots \quad (71)$$

Letting

$$n' = \frac{d(\ln\tau_w)}{d\left(\ln\frac{8V}{D}\right)} \quad \ldots\ldots\ldots\ldots\ldots \quad (72)$$

then

$$\left(-\frac{dv}{dr}\right)_w = \left(\frac{3n'+1}{4n'}\right)\left(\frac{8V}{D}\right) \quad \ldots\ldots\ldots\ldots\ldots \quad (73)$$

As a consequence of the Mooney analysis the shear rate at the wall is therefore derived directly.

The basic expression for n' may be integrated to yield

$$\ln\tau_w = n'\ln\left(\frac{8V}{D}\right) + \ln K' \quad \ldots\ldots\ldots\ldots\ldots \quad (74)$$

or

$$\tau_w = K'\left(\frac{8V}{D}\right)^{n'} \quad \ldots\ldots\ldots\ldots\ldots \quad (75)$$

This equation should hold for any time independent non-Newtonian regardless of the shear rate-shear stress relationship. The equation is similar to the equation for a pseudoplastic

$$\tau_w = K\left(-\frac{dv}{dr}\right)_w^n \quad \ldots\ldots\ldots\ldots\ldots \quad (76)$$

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9 "Explicit Formulas for Slip and Fluidity," by M. Mooney, Journal of Reology, Vol. 2, April, 1930, pp. 210-222.

10 "Notes on Transport Phenomena," by B. B. Bird, W. E. Stewart, and E. N. Lightfoot, Wiley & Sons, N. Y., 1958, p. 38.

11 "Flow of Non-Newtonian Fluids-Correlation of Laminar, Transition and Turbulent Flow Regions," by A. B. Metzner and J. C. Reed, Journal, Amer. Inst. of Chemical Engrs., Vol. 1, No. 4, December, 1950, pp. 434-440.

However it is to be noted that $\frac{8\,V}{D}$ is not the shear rate at the wall except for a Newtonian.

The value of n has been reported as approximately equal to n' in most engineering situations by Metzner.[8]

When n = n', the following relation obtains between K and K'.

$$K' = K\left(\frac{3\,n'+1}{4\,n'}\right)^{n'} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (77)$$

FORM OF HAGEN-POISEUILLE EQUATION FOR LAMINAR FLOW IN ROUND PIPE OR CAPILLARY

General.—A modified form of the familiar Hagen-Poiseuille equation may be derived for any of the fluids specified in the previous section. The flow equations which have been derived, together with the expression for τ_w, form the basis for the construction of a modified Hagen-Poiseuille equation.

Newtonian.—In the previous section it was shown that $\frac{8\,V}{D} = \frac{\tau_w}{\mu}$. In Appendix I there is given the relation $\frac{\Delta P}{4\,L} = \frac{\tau_w}{D}$. Eliminating τ_w, and solving for $\frac{\Delta P}{L}$,

$$\frac{\Delta P}{L} = \frac{32\,\mu\,V}{D^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (78)$$

This is the familiar Hagen-Poiseuille equation for Newtonians in laminar flow.

Bingham Plastic.—For laminar flow of Bingham Plastics the following relation (Eq. 39) was derived in the previous section

$$\frac{8\,V}{D} = \frac{\tau_w}{\eta}\left[1 - \frac{4}{3}\,\frac{\tau_y}{\tau_w} + \frac{1}{3}\left(\frac{\tau_y}{\tau_w}\right)^4\right] \quad \ldots\ldots\ldots\ldots \quad (79)$$

In Appendix I there is derived the expression

$$\frac{\Delta P}{4\,L} = \frac{\tau_w}{D}$$

The nature of the bracketed equation (Eq. 39) makes a solution difficult unless the last term in the brackets is neglected, which is possible when

$$\frac{\tau_y}{\tau_w} < 0.4$$

This results in the simplified expression

$$\frac{8\,V}{D} = \frac{\tau_w}{\eta}\left[1 - \frac{4}{3}\,\frac{\tau_y}{\tau_w}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (80)$$

When combined with the expression for τ_w there results a modified form of the Hagen-Poiseuille equation as given by Babbitt and Caldwell.[3,4,5]

$$\frac{\Delta P}{L} = \frac{32\,V\,\eta}{D^2}\left[1 + \frac{\tau_y\,D}{V\,\eta}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (81)$$

If $\eta = \mu$ and $\tau_y = 0$, this expression reduces to the Newtonian form.

Pseudoplastic.—For power function pseudoplastics, Eq. 82 was derived for laminar flow.

$$\tau_w = K\left(\frac{8\,V}{D}\right)^n \left(\frac{3\,n+1}{4\,n}\right)^n \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (82)$$

This is readily combined with the expression for τ_w derived in Appendix I.

$$\frac{\Delta P}{4\,L} = \frac{\tau_w}{D}$$

The resulting modified form of the Hagen-Poiseuille equation as given by Metzner[8] is

$$\frac{\Delta P}{L} = V^n \left[\frac{6n+2}{n}\right]^n \frac{4K}{D^{n+1}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (83)$$

If $n = 1$ and $K = \mu$, this reduces to Newtonian Form.

Any Time-Independent Fluid.—For all time independent non-Newtonian fluids it has been shown that

$$\tau_w = K'\left(\frac{8\,V}{D}\right)^{n'}$$

In Appendix I there is given $\frac{\tau_w}{D} = \frac{\Delta P}{4\,L}$. Combining,

$$\frac{\Delta P\,D}{4\,L} = K'\left(\frac{8\,V}{D}\right)^{n'} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (84)$$

This expression may be introduced into the Fanning friction factor equation

$$f = \frac{\frac{\Delta P\,D}{4\,L}}{\rho\,\frac{V^2}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (85)$$

or,

$$f = \frac{16\,K'\,(8)^{n'-1} V^{n'-2}}{\rho\,D^{n'}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (86)$$

and

$$\frac{\Delta P}{L} = \frac{32\,V^{n'} K'\,8^{n'-1}}{D^{n'+1}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (87)$$

This is the modified Hagen-Poiseuille equation for any time independent fluid as developed by Metzner.[8] If $n' = 1$ and $K' = \mu$, the equation reduces to the Newtonian form.

LAMINAR FLOW EQUATIONS FOR A ROTATIONAL VISCOMETER

General.—Flow equations for fluids in a rotational viscometer may be derived in much the same manner as those derived for a capillary. The results of course will not have the same general utility since they will not apply to round tubes.

In the following derivations, it will be assumed that the bob is stationary and the cup is rotating. The shear rate, $\frac{du}{dr}$, will be specified by

$$\frac{du}{dr} = \frac{dv_r}{dR} = R\frac{d\omega}{dR} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (88)$$

The boundary conditions will be specified such that $\omega = \Omega$ at the wall of the cup and $\omega = 0$ at the bob.

Newtonian.—For a Newtonian, an expression for $d\omega$ is obtained from the basic shear stress-shear rate relationship.

$$d\omega = \frac{\tau\, dR}{\mu R} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (89)$$

This expression is integrated from the bob to the cup

$$\int_0^{\Omega} d\omega = \int_{R_1}^{R_2} \frac{\tau}{\mu R}\, dR \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (90)$$

The solution of the right hand side requires that the relation between τ and R be known. This is provided by the equation developed in Appendix I.

$$\tau = \frac{M}{2\pi R^2 l} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (91)$$

Substituting and completing the integration

$$\Omega = \frac{M}{4\pi l \mu}\left[\frac{1}{R_1^2} - \frac{1}{R_2^2}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (92)$$

This is the laminar flow equation for Newtonians in a concentric viscometer with cup rotating and bob stationary.

The shear rate at the bob may be found from the basic shear stress-shear rate relationship

$$\left(\frac{dv_R}{dR}\right)_1 = \frac{\tau_1}{\mu} = \frac{M}{2\pi R_1^2 \mu l} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (93)$$

Bingham Plastic.—An expression for $d\omega$ is derived from the basic shear stress-shear rate relationship.

$$d\omega = \left[\frac{\tau}{\eta R} - \frac{\tau_y}{\eta R}\right] dR \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (94)$$

In this expression is substituted the relationship for τ found in Appendix I.

$$\tau = \frac{M}{2\pi R^2 l}$$

The result is integrated from the bob to the cup

$$\int_0^{\Omega} d\omega = \int_{R_1}^{R_2}\left[\frac{M}{2\pi R^3 l \eta} - \frac{\tau_y}{\eta}\right] dR \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (95)$$

The result is the flow equation for Bingham Plastics in laminar flow in a concentric viscometer as given by G. E. Alves[6,7] and H. Green.[12]

$$\Omega = \frac{M}{4\pi l \eta}\left[\frac{1}{R_1^2} - \frac{1}{R_2^2}\right] - \frac{\tau_y}{\eta}\ln\left(\frac{R_2}{R_1}\right) \quad \ldots\ldots\ldots\ldots (96)$$

Eq. 96 may be combined with the fundamental equation for shear stress-shear rate relationship to determine the shear rate at the bob.

Thus,

$$\left(\frac{dv_R}{dR}\right)_1 = \frac{\tau_1}{\eta} - \frac{\tau_y}{\eta} \quad \ldots\ldots\ldots\ldots\ldots\ldots (97)$$

or

$$\left(\frac{dv_R}{dR}\right)_1 = \frac{M}{2\pi\eta R_1^2 l} - \frac{\tau_y}{\eta} \quad \ldots\ldots\ldots\ldots (98)$$

Pseudoplastic.—The basic equation for the pseudoplastic is

$$\tau = K\left(R\frac{d\omega}{dR}\right)^n \quad \ldots\ldots\ldots\ldots\ldots (99)$$

This equation may be combined with the equation from Appendix I

$$\tau = \frac{M}{2\pi R^2 l}$$

The result is solved in terms of $\frac{d\omega}{dR}$

Solving for $d\omega$ and integrating from the bob to the cup yields

$$\int_0^{\Omega} d\omega = \int_{R_1}^{R_2}\left(\frac{M}{2\pi K l}\right)^{\frac{1}{n}}\left(\frac{1}{R^{2+n}}\right)^{\frac{1}{n}} dR \quad \ldots\ldots\ldots\ldots (100)$$

Completing the integration yields

$$\Omega = \left(\frac{M}{2\pi K l}\right)^{\frac{1}{n}}\left(\frac{n}{2}\right)\left[\frac{1}{R_1^{2/n}} - \frac{1}{R_2^{2/n}}\right] \quad \ldots\ldots\ldots (101)$$

This is the basic flow equation for power function pseudoplastics in laminar flow in rotational viscometers with rotating cup and stationary bob.

It is demonstrated in Appendix II that n has the special relation

$$n = \frac{d(\ln \tau_1)}{d(\ln \Omega)}$$

Once again the flow equation may be combined with the shear rate-shear stress relation to derive the shear rate at the bob. The relation between τ and M given in Appendix I is also required

$$\left(\frac{dv_R}{dR}\right)_1 = \left(\frac{\tau_1}{K}\right)^{\frac{1}{n}} = \left(\frac{M}{2\pi R_1^2 l K}\right)^{\frac{1}{n}} \quad \ldots\ldots\ldots\ldots (102)$$

12 "Industrial Rheology and Rheological Structures," by H. Green, John Wiley and Sons, New York, 1949.

Substituting in the flow equation

$$\Omega = \left(\frac{dv_R}{dR}\right)_1 \left(R_1^{2/n}\right)\left(\frac{n}{2}\right)\left(\frac{1}{R_1^{2/n}} - \frac{1}{R_2^{2/n}}\right) \quad \ldots\ldots (103)$$

Solving for the shear rate at the bob

$$\left(\frac{dv_R}{dR}\right)_1 = \frac{2\,\Omega}{n\left[1 - \left(\frac{R_1}{R_2}\right)^{2/n}\right]} \quad \ldots\ldots (104)$$

Any Time-Independent Fluid.—To derive a flow equation for any fluid, the shear stress-shear rate relationship must be kept in a generalized form.

$$\frac{dv_R}{dR} = G(\tau) = R\frac{d\omega}{dR} = \frac{d\omega}{d(\ln R)} \quad \ldots\ldots (105)$$

From Appendix I it is known that

$$\tau = \frac{M}{2\pi R^2 l}$$

Therefore,

$$d\tau = -\frac{M\,dR}{\pi R^3 l} = -\frac{2\tau\,dR}{R} \quad \ldots\ldots (106)$$

or,

$$d(\ln \tau) = -2\,d(\ln R) \quad \ldots\ldots (107)$$

Thus,

$$G(\tau) = -\frac{2\,d\omega}{d(\ln \tau)} \quad \ldots\ldots (108)$$

This equation is solved for $d\omega$ and integrated from the bob to the cup.

$$\int_0^{\Omega} d\omega = -\int_{\tau_1}^{\tau_2} \frac{G(\tau)\,d\tau}{2\tau} \quad \ldots\ldots (109)$$

or

$$\Omega = \frac{1}{2}\int_{\tau_2}^{\tau_1} \frac{G(\tau)\,d\tau}{\tau} \quad \ldots\ldots (110)$$

The relationship $S = \frac{R_2}{R_1}$ is now introduced

From Appendix I,

$$S^2 = \left(\frac{R_2}{R_1}\right)^2 = \left(\frac{\tau_1}{\tau_2}\right) \quad \ldots\ldots (111)$$

Eq. 111 may be rewritten

$$\Omega = \frac{1}{2}\int_{\frac{\tau_1}{S^2}}^{\tau_1} \frac{G(\tau)}{\tau}\,d\tau \quad \ldots\ldots (112)$$

Differentiating this expression with respect to τ.

$$\frac{\partial \Omega}{\partial \tau_1} = \frac{1}{2}\left[\frac{G(\tau_1)}{\tau_1} - \frac{1}{S^2}\,\frac{G(\tau_1/S^2)}{\tau_1/S^2}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots (113)$$

This is simplified to

$$\frac{\partial \Omega}{\partial \tau_1} = \frac{1}{2\,\tau_1}\,\left[G(\tau_1) - G(\tau_2)\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots (114)$$

Eq. 114 is that given by I. M. Krieger and H. Elrod.[13,14] The solution to Eq. 114 is given in considerable detail and will not be repeated here. They derive an asymptotic solution by means of the Euler-Maclaurin Integration formula. The result is an equation which converges sufficiently for S greater than 1.2.

$$\Omega = \frac{G(\tau 1)\,\ln S}{\left[1 + m \ln S + \frac{1}{3} m^2 (\ln S)^2 + \frac{(4\,n\,S)^2}{3}\,\frac{dm}{d(\ln \tau_1)} + \ldots\right]} \quad \ldots\ldots (115)$$

in which $m = \frac{1}{n} = \frac{d(\ln \Omega)}{d(\ln \tau 1)}$

Since by definition, $G(\tau_1) = \left(\frac{dv_R}{dR}\right)_1$, the shear rate at the bob is found directly from the same equation

$$\left(\frac{dv_R}{dR}\right)_1 = \frac{\Omega}{\ln S}\,\left[1 + m \ln S + \frac{1}{3} m^2 (\ln S)^2 + \frac{(\ln S)^2}{3}\,\frac{d\,m}{d(\ln \tau_1)} + \ldots\right] \ldots (116)$$

When the derivative term in the brackets on the right is sufficiently small, this equation may be simplified to

$$\left(\frac{dv_R}{dR}\right)_1 = \frac{\Omega}{\ln S}\,\left[1 + m \ln S + \frac{1}{3} m^2 (\ln S)^2\right] \quad \ldots\ldots\ldots\ldots (117)$$

J. S. Rankine has demonstrated that the flow equation for pseudoplastics given previously is mathematically equivalent to this equation.[15] This equivalence is shown in Appendix III.

PRESSURE DROP, FRICTION FACTOR, AND REYNOLDS NUMBER RELATIONSHIPS

General.—Pressure drop, friction factor, and Reynolds Number relationships are described in this section. In effect these relationships are still concerned with laminar flow. Previously in the section concerned with modified Hagen-Poiseuille equations pressure drop relationships were described in detail. These equations have limited use in application since some technique

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13 "Direct Determination of Flow Curves of Non-Newtonian Fluids II, Shearing Rates in the Concentric Cylinder Viscometer," by I. M. Krieger and H. Elrod, Journal of Applied Physics, Vol. 24, No. 2, 1953, pp. 234-236.

14 "Direct Determination of Flow Curves of Non-Newtonian Fluids III, Standardized Treatment of Viscometric Data," by I. M. Krieger and S. H. Maron, Journal of Applied Physics, Vol. 25, 1954, p. 72.

15 M. Ch. E. Thesis, by J. S. Rankin, Univ. of Delaware, Newark, Del., June, 1955.

must be at hand to qualify the flow as laminar or turbulent. In the latter case an empirical equation is available to calculate the Fanning friction factor from the Reynolds Number. As before, the relationships are general and reduce to the Newtonian as a special case.

Newtonian.—For a Newtonian fluid in laminar flow, the pressure drop is given as a function of several values as follows

$$\frac{\Delta P}{L} = \Phi_1 \ (D, V, \rho, \mu) \quad \ldots\ldots\ldots\ldots\ldots\ldots (118)$$

By familiar methods of dimensional analysis it is shown that.

$$\frac{\Delta P}{L} = \frac{K_1 V^2 \rho}{D} \left(\frac{V D \rho}{\mu}\right)^{h-2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (119)$$

Since by definition, $\frac{\Delta P}{L} = \frac{2 f \rho V^2}{D}$ it follows that $2 f = K_1 \left(N_{RE}\right)^{n-2}$, where $N_{RE} = \frac{V D \rho}{\mu}$, or more generally, $f = \Phi_2 \left(N_{RE}\right)$.

By comparison with the Hagen-Poiseuille equation given previously the familiar relationship for Fanning friction factor and Reynolds Number is obtained, $f = 16/N_{RE}$.

From the nature of the solution, this equation is limited to laminar flow.

Bingham Plastic.—For a Bingham Plastic the pressure drop relationship becomes

$$\frac{\Delta P}{L} = \Phi_3 \left(D, V, \rho, \eta, \tau_y\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots (120)$$

Conventional methods for dimensional analysis yield the result

$$\frac{\Delta P}{L} = K_3 \left(\frac{\rho V^2}{D}\right) \left(\frac{V D \rho}{\eta}\right)^{n-2} \left(\frac{D^2 \rho \tau_y}{\eta^2}\right)^b \quad \ldots\ldots\ldots\ldots\ldots\ldots (121)$$

By analogy to the Newtonian

$$f = K_3 \left(N_{RE}\right)^{n-2} \left(N_{HE}\right)^b \quad \ldots\ldots\ldots\ldots\ldots\ldots (122)$$

Where $N_{RE} = \frac{V D \rho}{\eta}$, $N_{HE} = \frac{D^2 \rho \tau_y}{\eta^2}$ = Hedstrom Number. This may be written

$$f = \Phi_4 \left(N_{RE}, N_{HE}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots (123)$$

An exact expression can be determined relating the friction factor, Reynolds Number, and Hedstrom Number. This has been done by A. Perkins and J. J. Glick,[16] with the result

$$\frac{1}{N_{RE}} = \frac{f}{16} - \frac{1}{6}\left(\frac{N_{HE}}{N_{RE}^2}\right) + \frac{1}{3}\frac{1}{f^3}\left(\frac{N_{HE}^4}{N_{RE}^8}\right) \quad \ldots\ldots\ldots\ldots (124)$$

The derivation of this expression, which is limited to laminar flow, is given in Appendix IV.

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16 B.Ch. E. Thesis, by A. Perkins and J. J. Glick, Univ. of Delaware, Newark, Del., June, 1954.

Pseudoplastics.—Dimensional analysis does not lend itself to the pseudoplastic. However, it may be assumed that for laminar flow, $f = 16/N_{RE}$.

By definition,

$$f = \frac{\frac{\Delta P\, D}{4\, L}}{\rho \frac{V^2}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (125)$$

These equations may now be combined with the modified Hagen-Poiseuille equation for psuedoplastics.

$$\frac{\Delta P}{L} = V^n \left[\frac{6\ n+2}{n}\right]^n \frac{4\ K}{D^{n+1}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (126)$$

The result is

$$N_{RE} = \frac{8\ V^{2-n}\ D^n\ \rho}{K \left[\frac{6_n + 2}{n}\right]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (127)$$

Any Time-Independent Fluid.—As with the pseudoplastic fluid, the generalized fluid does not lend itself to dimensional analysis. However, the assumption may be made that for laminar flow $f = 16/N_{RE}$.

Also, by definition,

$$f = \frac{\frac{\Delta P\, D}{4\, L}}{\rho \frac{V^2}{2}}$$

These equations may be then combined with the modified Hagen-Poiseuille equation for fluids of unspecified shear rate-shear stress relationship.

$$\frac{\Delta P}{L} = \frac{4\ K'}{D} \left(\frac{8\ V}{D}\right)^{n'} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (128)$$

The result is a modified and generalized Reynolds Number for all time independent fluids as reported by Metzner.[8]

$$N_{RE} = \frac{D^{n'}\ \rho\ V^{2-n'}}{K'\ 8^{n'-1}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (129)$$

SUMMARY

The intention of this paper has been to present a formal compilation of the methods of solving equations which might be used to analyze the flow behavior of sewage sludges.

At least two useful mathematical models of shear stress-shear rate relationships are available as a starting point in these derivations. The Bingham Plastic or Pseudoplastic model can of course be utilized when the experimental evidence indicates their possible application. Alternatively the more generalized

equations for any time-independent fluids may be used, and for this reason may be of somewhat broader application.

ACKNOWLEDGMENTS

Grateful acknowledgment is given that this paper was made possible by Grant RG-6435 of the National Institutes of Health, United States Public Health Service. Much of this report was prepared from the author's informal lecture notes by Harold Read, graduate assistant.

APPENDIX I.—SHEAR STRESS AT VARYING RADIAL DISTANCES

Capillary and Round Pipes.—Regardless of the fluid, it is possible to isolate the free body of a cylindrical element of fluid. (The axis of the cylinder is parallel to the axis of the tube.)

Making an equilibrium force balance on a cylinder of radius, r and length, L.

$$\tau(2\pi r)L = \Delta P \pi r^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (130)$$

or

$$\tau = \frac{r \Delta P}{2 L} \quad \ldots\ldots\ldots\ldots\ldots\ldots (131)$$

If the radius in question is that of the pipe then

$$\tau_w = \frac{\Delta P D}{4 L} = \frac{r_w \Delta P}{2 L} \quad \ldots\ldots\ldots\ldots\ldots\ldots (132)$$

By comparison of these two formulas

$$\frac{\tau}{\tau_w} = \frac{r}{r_w} \quad \ldots\ldots\ldots\ldots\ldots\ldots (133)$$

Rotational Viscometer.—In a rotational viscometer the cylindrical section is taken so that its radius R is greater than that of the bob but less than that of the cup. A force balance yields

$$M = \tau(2\pi R l)R \quad \ldots\ldots\ldots\ldots\ldots\ldots (134)$$

or

$$\tau = \frac{M}{2\pi R^2 l} \quad \ldots\ldots\ldots\ldots\ldots\ldots (135)$$

At the bob this becomes

$$\tau_1 = \frac{M}{2\pi R_1^2 l} \quad \ldots\ldots\ldots\ldots\ldots\ldots (136)$$

In general it may be seen that

$$\frac{\tau_1}{\tau_2} = \frac{R_2^2}{R_1^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (137)$$

APPENDIX II.—EQUATION FOR n IN ROTATIONAL VISCOMETER

In the section titled "Laminar Flow Equations for a Rotational Viscometer," the following expression (Eq. 114) is given.

$$\frac{\partial \Omega}{\partial \tau_1} = \frac{1}{2\,\tau_1} \left[G(\tau_1) - G(\tau_2)\right]$$

By definition this may be rewritten

$$\frac{\partial \Omega}{\partial \tau_1} = \frac{1}{2\,\tau_1} \left[\frac{\tau_1}{\mu_{a_1}} - \frac{\tau_2}{\mu_{a_2}}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots (138)$$

or

$$\frac{\partial \Omega}{\partial \tau_1} = \frac{1}{2\,\mu_{a_1}} \left[1 - \frac{\tau_2}{\tau_1}\,\frac{\mu_{a1}}{\mu_{a_2}}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots (139)$$

By definition of the power function relationship for a pseudoplastic

$$\frac{\mu_{a_1}}{\mu_{a_2}} = \frac{\tau_1}{\tau_2} \left(\frac{\tau_2}{\tau_1}\right)^{1/n} \quad \ldots\ldots\ldots\ldots\ldots\ldots (140)$$

From Appendix I,

$$\frac{\tau_2}{\tau_1} = \frac{R_1^2}{R_2^2}$$

Combining,

$$\frac{\partial \Omega}{\partial \tau_1} = \frac{1}{2\,\mu_{a_1}} \left[1 - \left(\frac{R_1}{R_2}\right)^{2/n}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots (141)$$

Now in the section titled "Laminar Flow Equations for a Rotational Viscometer," the following flow equation (Eq. 104) for a pseudoplastic was derived

$$\left(\frac{dv_R}{dR}\right)_1 = \frac{2\,\Omega}{n\left[1 - \left(\frac{R_1}{R_2}\right)^{2/n}\right]}$$

This expression may be rewritten

$$\frac{\Omega}{n\,\tau_1} = \frac{1}{2\,\mu_{a_1}} \left[1 - \left(\frac{R_1}{R_2}\right)^{2/n}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots (142)$$

It is therefore seen that

$$\frac{\partial \Omega}{\partial \tau_1} = \frac{\Omega}{n\,\tau_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots (143)$$

or

$$n = \frac{d(\ln \tau_1)}{d(\ln \Omega)} \quad \ldots\ldots\ldots\ldots\ldots\ldots (144)$$

APPENDIX III.—EQUIVALENCE OF EQUATIONS

$$\left(\frac{dv_R}{dR}\right)_1 = \frac{\Omega}{\ln S}\left[1 + m \ln S + \frac{1}{3} m^2 (\ln S)^2\right] \quad \ldots\ldots\ldots\ldots (145)$$

and

$$\frac{dv_R}{dR} = \frac{2\,\Omega}{n\left[1 - \left(\frac{R_1}{R_2}\right)^{2/n}\right]} \quad \ldots\ldots\ldots\ldots\ldots (146)$$

Given Eq. 146 introduce

$$m = \frac{1}{n}, \; S = \frac{R_2}{R_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots (147)$$

and

$$\left(\frac{dv_R}{dR}\right)_1 = \frac{2\,m\,\Omega}{\left[1 - \left(\frac{1}{S^2}\right)^m\right]} \quad \ldots\ldots\ldots\ldots\ldots\ldots (148)$$

Expand $\left(\frac{1}{S^2}\right)^m$ as a Maclaurin series

$$\left(\frac{1}{S^2}\right)^m = 1 + m \ln \left(\frac{1}{S^2}\right) + \frac{m^2 \left(\ln \frac{1}{S^2}\right)^2}{2\,!} + \frac{m^3 \left(\ln \frac{1}{S^2}\right)^3}{3\,!} + \ldots\ldots\ldots (149)$$

and

$$\left(\frac{1}{S^2}\right)^m = 1 - 2\,m \ln S + 2\,m^2 (\ln S)^2 - \frac{4}{3} m^3 (\ln S)^3 + \ldots\ldots\ldots (150)$$

The quantity in brackets becomes

$$\left[1 - \left(\frac{1}{S^2}\right)^m\right] = 2\,m \ln S - 2\,m^2 (\ln S)^2 + \frac{4}{3} m^3 (\ln S)^3 + \ldots\ldots\ldots (151)$$

The pseudoplastic flow equation is now written

$$\left(\frac{dv_R}{dR}\right)_1 = \frac{\Omega}{\ln S\left[1 - m \ln S + \frac{2}{3} m^2 (\ln S)^2 + \ldots\right]} \quad \ldots\ldots\ldots (152)$$

The quantity in the brackets is divided into Ω and there results

$$\left(\frac{dv_R}{dR}\right)_1 = \frac{\Omega}{\ln S}\left[1 + m \ln S + \frac{1}{3} m^2 (\ln S)^2 + \ldots\right] \quad \ldots\ldots\ldots (153)$$

This completes the proof of equivalence.

APPENDIX IV.—RELATION BETWEEN FANNING FRICTION FACTOR, REYNOLDS NUMBER, AND HEDSTROM NUMBER.

In the last section of the paper it was shown by dimensional analysis that f was a function of N_{HE} and N_{RE} (Eq. 123).

$$f = \Phi_4 \left(N_{RE} , N_{HE} \right)$$

where

$$N_{RE} = \frac{D V \rho}{\eta}, \quad N_{HE} = \frac{D^2 \rho \tau_y}{\eta^2}, \quad f = \frac{2 \tau_w}{\rho V^2} \quad \ldots\ldots\ldots\ldots (154)$$

To establish the exact nature of this relationship it is necessary to return to the Buckingham equation (Eq. 39), which was derived in the section titled "Laminar Flow Equations for the Capillary Viscometer."

$$\frac{8 V}{D} = \frac{\tau_w}{\eta} \left[1 - \frac{4}{3} \frac{\tau_y}{\tau_w} + \frac{1}{3} \left(\frac{\tau_y}{\tau_w} \right)^4 \right]$$

This may be written

$$\frac{8 V}{D} = \frac{\rho v^2 f}{2 \eta} \left[1 - \frac{4}{3} \frac{\tau_y}{\tau_w} + \frac{1}{3} \left(\frac{\tau_y}{\tau_w} \right)^4 \right] \quad \ldots\ldots\ldots\ldots (155)$$

or

$$\frac{\eta}{V D \rho} = \frac{1}{N_{RE}} = \frac{f}{16} \left[1 - \frac{4}{3} \frac{\tau_y}{\tau_w} + \frac{1}{3} \left(\frac{\tau_y}{\tau_w} \right)^4 \right] \quad \ldots\ldots\ldots\ldots (156)$$

Now it may also be shown that

$$\frac{\tau_y}{\tau_w} = \frac{2}{f} \left(\frac{N_{HE}}{N_{RE}^2} \right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (157)$$

Substituting and simplifying

$$\frac{1}{N_{RE}} = \frac{f}{16} - \frac{1}{6} \frac{N_{HE}}{N_{RE}^2} + \frac{1}{3 f^3} \frac{N_{HE}^4}{N_{RE}^8} \quad \ldots\ldots\ldots\ldots\ldots (158)$$

APPENDIX V.—NOTATION

Any consistent set of units may be used. The following units specified below are in the English gravitational system.

NOMENCLATURE	DESCRIPTION	DIMENSION
A	Area	L^2
b	Exponent used in dimensional analysis	None
d	Differential operator	None
$\frac{du}{dy}$	Shear rate in general terms	T^{-1}

$\frac{dv}{dR}$	Shear rate in pipe or capillary	T^{-1}
$\left(\frac{dv}{dR}\right)_w$	Shear rate at wall of pipe or capillary	T^{-1}
$\frac{dv_R}{dR}$	Shear rate in rotational viscometer	T^{-1}
$\left(\frac{dv_R}{dR}\right)_1$	Shear rate at bob in rotational viscometer	T^{-1}
D	Diameter of pipe or capillary	L
f	Fanning friction factor	None
F	Denotes functional relationship	None
g	Acceleration due to gravity	$L\ T^{-2}$
G	Denote functional relationship	None
h	Exponent used in dimensional analysis	None
k_1, k_2	Proportionality constant used in dimensional analysis	None
K	Fluid consistency index for power function pseudoplastics	$F\ T^n\ L^{-2}$
K'	Fluid consistency index for fluids of unspecified shear stress-shear rate relationships	$F\ T^{n'}\ L^{-2}$
l	Equivalent length of viscometer bob	L
ln	Natural logarithm	None
L	Length of pipe or capillary	L
m	Inverse of n	None
M	Torque	F L
n	Flow behavior index for power function pseudoplastics	None
n'	Flow behavior index for fluids of unspecified shear stress-shear rate relationships	None
N_{HE}	Hedstrom number	None
N_{RE}	Reynolds number	None
P	Pressure drop	$F\ L^{-2}$
q_1	Volumetric flow rate in plug Bingham Plastic	$L^3\ T^{-1}$
q_2	Volumetric flow rate outside of plug Bingham Plastic	$L^3\ T^{-1}$
Q	Volumetric flow rate	$L^3\ T^{-1}$

r	Radial distance in pipe or capillary	L
r_i	Radial distance from centerline of pipe	L
r_c	Radial distance to centerline of pipe or capillary	L
r_w	Radial distance to wall of pipe or Capillary	L
r_y	Radius at which τ_y is reached	L
R	Radial distance in rotational viscometer	L
R_1	Radius of bob in rotational viscometer	L
R_2	Radius of cup in rotational viscometer	L
$R\frac{d\omega}{dR}$	Shear rate in rotational viscometer	L
S	Ratio of R_2 to R_1	None
u	Local velocity, general	$L\ T^{-1}$
v	Local velocity in pipe of capillary	$L\ T^{-1}$
v_i	Velocity at $r = r_i$	$L\ T^{-1}$
v_y	Velocity at outer edge of plug	$L\ T^{-1}$
v_w	Velocity at pipe or capillary wall	$L\ T^{-1}$
v_R	Local velocity in rotational viscometer	$L\ T^{-1}$
V	Average velocity in capillary or pipe	$L\ T^{-1}$
x	Substitution for group $\frac{2\ V}{D}$	T^{-1}
y	Lineal distance	L
η	Coefficient of rigidity of a Bingham Plastic	$F\ T\ L^{-3}$
Φ	Denotes functional relationship	None
ρ	Mass density of a fluid	$F\ L^{-3}$
μ	Viscosity of a Newtonian fluid	$F\ T\ L^{-2}$
μ_a	Apparent viscosity	$F\ L^{-2}\ T$
μ_{a_1}	Apparent viscosity at bob	$F\ L^{-2}\ T$
μ_{a_2}	Apparent viscosity at cup	$F\ L^{-2}\ T$
τ	Shear stress	$F\ L^{-2}$
τ_1	Shear stress at the bob	$F\ L^{-2}$
τ_2	Shear stress at the cup	$F\ L^{-2}$
ω	Angular velocity in rotational viscometer	T^{-1}
Ω	Angular velocity at the cup	T^{-1}

Journal of the
SANITARY ENGINEERING DIVISION
Proceedings of the American Society of Civil Engineers

DISCUSSION

Note.—This paper is a part of the copyrighted Journal of the Sanitary Engineering Division, Proceedings of the American Society of Civil Engineers, Vol. 86, No. SA 6, November, 1960.

REFUSE VOLUME REDUCTION IN A SANITARY LANDFILL[a]

Closure by Solid Wastes Engineering Section, of the Sanitary Engineering Research Committee, of the Sanitary Engineering Division

Closure.—The discussion by Desso T. Mitchell includes valuable suggestions for further landfill research. It is interesting to note that certain questions raised concerning how a landfill becomes stable and the factors that influence stability are currently being investigated by the University of Southern California as a result of a U. S. Public Health Service research grant. Robert C. Merz, the Project Director, in cooperation with the Los Angeles County Sanitation District, has constructed at the Spadra landfill, six full-scale, 100 ft by 100 ft area and 20 ft depth, test cells. The cells are arranged so as to determine the effect of moisture content, earth admixture, aeration, compaction, nutrients, surface plant growth, etc. An instrument and sampling test well was installed in the center of each test cell for collection of gas, liquid, and solid waste samples at various depths in each cell. Instrumentation has also been installed for measuring temperature, refuse weight and settlement. This research study should be of value in answering some basic questions concerning refuse volume reduction.

Considerable empirical landfill operating experience is available at existing sites throughout the nation. To tap this resource, the Solid Wastes Engineering Section is currently preparing a summary report describing the results of its questionnaire survey of existing municipal landfills. Mr. Mitchell's observations on the value of long-period study of landfills is particularly significant. The results of routine sampling of landfills, measurement of surface and volume reduction should be of interest to all engineers involved with refuse disposal and land reclamation. The stimulation of improved refuse disposal practices is dependent upon "filling in" the meager technical knowledge concerning landfill phenomena. The construction of sanitary landfills in metropolitan communities is restricted by the limited available land and the high costs of property. It is apparent that a knowledge of efficient operating practices would enable either the reuse of the same area for further refuse disposal or the achievement of greater disposal volumes during the initial construction period.

[a] November, 1959, Twenty Sixth Progress Report of the Committee on Sanitary Engineering Research of the Sanitary Engineering Division.

DIFFUSION IN A SECTIONALLY HOMOGENEOUS ESTUARY[a]

Discussion by Richard Kent

J. M. JORDAAN, JR.[7]—The writer would like to present a few observations on the initial diffusion stage. The author excluded this stage from consideration, nevertheless, the writer feels it is important enough in its bearing on the analysis of diffusion time and space distributions to warrant mentioning.

In studying one dimensional turbulent diffusion in a uniform field, the first approach is to consider the process as analogous to classical heat diffusion. The eddy diffusivity is then found to be proportional to a mechanical eddy viscosity, expressed as a representative displacement multiplied by a velocity.[8] In the case of tidal oscillation, it would be the longitudinal range of the fluid particle displacement times the R.M.S. value of the velocity. Seen in this manner, the eddy diffusivity appears to be dependent only on the intensity of the turbulence generated with the boundaries and independent of the time-space history of the diffusion process or of the diffusant concentration, under the assumed homogeneous, well-mixed estuary conditions.

It has been found by G. I. Taylor, de Feriet, Frenkiel, Goldstein, and others, that this assumption is not strictly true in turbulent diffusion where diffusion distances from the source are of the same order as the eddy scale of the turbulence. The reason for this is tied up with the finite velocities at which a property may be transported from eddy to eddy.[9] In heat diffusion, the property (heat) is relayed by much faster rates of transfer between molecules than the rate of progression of any sensible temperature increase, but this is not the case in the initial stage of turbulent diffusion. The turbulent diffusion equation eventually merges into the classical diffusion equation. Thus, one can avoid the complication of a slowly varying diffusion coefficient in experimental analysis by subtracting an appropriate constant (time or distance) and treating the process as ideal diffusion from new virtual time and distance origins.

One-dimensional spatial distribution of diffusivity may be readily obtained from unsteady state data by graphical differentiation of the curves of concentration versus time and distance. This is an exact method. The diffusivity is given by

$$K_{x'\,t} = \left[\int_0^x \frac{\partial c}{\partial t}\,dx - \int_0^\infty \frac{\partial c}{\partial t}\,dx\right] \Big/ \frac{\partial c}{\partial x} \quad \ldots\ldots\ldots\ldots (67)$$

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[a] March, 1960, by Richard Kent.

[7] Head, Hydr. Section, Natl. Mech. Engrg. Research Inst., South African Council for Scientific and Industrial Research, Pretoria, South Africa.

[8] "The Diffusion of Two Fluids of Different Density in a Homogeneous Turbulent Field," by D. R. F. Harleman, J. M. Jordaan Jr., and J. D. Lin, Mass. Instit., Tech. Hydrodynamics Lab., T. R. No. 31, February, 1959, p. 64.

[9] "On Diffusion Discontinuous Movements and On the Telegraph Equation," by S. Goldstein, Quarterly Journal of Mechanics and Applied Mathematics, Vol. 4, Part 2, 1951, pp. 129-156.

Results for the unsteady state diffusion by homogeneous turbulence of an initial step function of concentration in a one dimensional uniform turbulent field,[8] showed that K was practically independent of time but decreased with distance from the initial discontinuity in concentration, which was, in effect, a source at constant potential for $t > 0$. Assuming classical diffusion, an apparent diffusivity for small distances was found to be two to three times greater than the local diffusivity further away. This trend of variation of diffusivity with distance under uniform density and uniform turbulence was also obtained in tests where a density gradient longitudinally existed. No differentiation between the diffusing of salt solutions and control tests using dye and buoyant tracer spheres was obtained in this respect, that is, all showed a distance dependence of the diffusion coefficient so that the phenomenon could not be ascribed to interactions of molecular and turbulent diffusion processes.

Steady state tests[10] were subsequently performed where dye or saline water was introduced through a manifold uniformly across a vertical cross section so as to diffuse one-dimensionally against a slowly moving horizontal current. The data were plotted on semi-log paper and in all cases it was evident that a local increase of diffusivity occurred at the zone near the manifold that was not ascribable to any experimental effect. The diffusivity was computed from

$$K_x = \left(V_f\, C\right) \Big/ \frac{dc}{dx} \quad \ldots\ldots\ldots\ldots\ldots\ldots (68)$$

in which V_f is the current velocity, C refers to the concentration, and K_x denotes the diffusivity.

The higher diffusivity near the diffusion origin for both zero and finite density gradients was ascribed to its dependence on the initial concentration fluctuation intensity, or of the temporal mean concentration itself. After the concentration gradients became reduced, the diffusion could be treated as from a somewhat displaced, new virtual diffusion origin, thus neglecting the zone where the diffusivity was found to be distance dependent.

In estuarine mixing this local increase of diffusivity (evident also from results presented by the author) is important for the initial dilution of effluents and resulting density adjustment which would influence the future history to a marked extent. It would be highly desirable to study the initial phase exhaustively and to tie it up with eddy scale and tidal period for the sectionally homogeneous estuary case.

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10 "Mass-Transfer Rates in a Turbulent Fluid Body," by Jan M. Jordaan Jr., Sc. D. Thesis, Mass. Instit. of Tech., Dept. of Civ. and San. Engrg., June, 1958, pp. 124-128.

FUNDAMENTAL CONSIDERATIONS IN HIGH RATE DIGESTION[a]

Discussion by M. T. Garrett, Jr.

M. T. GARRETT, JR.[24]—The authors have stressed the value of first order reaction kinetics as a basis for predicting the effects of increased organic loadings or reduced detention times or a combination of the two. They have pointed out that at low detention times, approximately 3 days, the process fails and no longer conforms to first order kinetics. They have indicated that according to the overall equation,

$$\text{ORGANIC MATTER} + \text{BACTERIA} \rightarrow CH_4 + CO_2,$$

the reaction might be second order because of the two reactants. It was stated that since the bacteria are not consumed in the reaction, the reaction is actually first order in character.

Because the bacteria are not consumed, they must be a product of the reaction; the role of catalyst might be assigned to the bacteria and the equation written as

$$\text{ORGANIC MATTER} \xrightarrow{\text{Bacteria}} CH_4 + CO_2.$$

This form of the equation leaves only one reactant so that the reaction may be considered first order with respect to the organic matter.

If the concentration of the catalyst, that is, the bacteria, is important, the rate equation is

$$\frac{-dC}{dt} = k\,C\,(\text{Bacteria}) \quad \ldots\ldots\ldots\ldots\ldots\ldots (1a)$$

in which t is time (commonly measured in days) for sludge digestion, C is the concentration of digestible solids, and k is the rate constant. The concentration of bacteria may be combined with k to give a new rate constant k' so that,

$$\frac{-dC}{dt} = k'\,C \quad \ldots\ldots\ldots\ldots\ldots\ldots (1b)$$

For a continuously fed, mixed digester, the solids destroyed are equal to the rate constant times the solids in the digester. The equation for the operation is

$$(C_o - C)Q = k'\,C\,V \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

in which C_o is the concentration of digestible solids in the feed, Q is the rate of flow into and out of the digester, and V is the digester volume. The equation may be rearranged to read

$$\frac{C}{(C_o - C)} = \frac{Q}{k'\,V} \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

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[a] March, 1960, by Clair N. Sawyer and Jay S. Gumbling.

[24] Asst. Supt. of Sewage Treatment Plants, Houston, Tex.

The progress of digestion is normally followed by the destruction of volatile solids. The volatile solids destroyed are readily measured. The digestible volatile solids remaining, C, is unknown so that Eq. 3 cannot be solved directly. To overcome this difficulty, let x be the concentration of undigestible volatile solids and C_V equal the concentration of volatile solids in the sludge.

Then

$$C = C_V - x \quad \ldots\ldots\ldots\ldots\ldots\ldots (4a)$$

and

$$C_O = C_{V_O} - x \quad \ldots\ldots\ldots\ldots\ldots\ldots (4b)$$

Substituting these values in Eq. 3,

$$\frac{C_V - x}{(C_{V_O} - x) - (C_V - x)} = \frac{Q}{k' V} \quad \ldots\ldots\ldots\ldots (5a)$$

and

$$\frac{C_V - x}{C_{V_O} - C_V} = \frac{Q}{k' V} \quad \ldots\ldots\ldots\ldots\ldots\ldots (5b)$$

When C_V is small, the equation approaches

$$\frac{C_V - x}{C_{V_O}} = \frac{Q}{k' V} \quad \ldots\ldots\ldots\ldots\ldots\ldots (6a)$$

from which,

$$\frac{C_V}{C_{V_O}} = \frac{x}{C_{V_O}} + \frac{Q}{k' V} \quad \ldots\ldots\ldots\ldots\ldots\ldots (6b)$$

A plot of C_V/C_{V_O}, the fraction of volatile solids remaining, versus Q/V give a nearly straight line with an intercept at x/C_{V_O}, the undigestible fraction of the feed, and a slope of approximately 1/k'. The value of x/C_{V_O} may be determined by extrapolation or other more precise means. The value of k' should be computed from Eq. 5b because Eq. 6b is an approximation.

Data presented by the authors, by N. Sawyer and H. K. Roy,[25] and by W. N. Torpey,[26] F. ASCE are shown plotted in this manner in Fig. 11. The raw sludges were in the range of 75% volatile and temperatures were in the range of 85° to 98°F. A distinct difference is apparent in the fraction of undigestible solids in the primary activated sludge mixture as compared to the primary sludge. However, a difference in the rate constant, k', is not so obvious. The data of Mr. Torpey's are sufficiently scattered to allow quite a range of values of k' to be selected.

If C and $C_O - C$ are measured in terms of gas production, then $C_O - C$ is the gas produced in the digester, and C is the potential gas production remaining in the sludge withdrawn. Eq. 3 may be rearranged into the form,

$$k' = \frac{(C_O - C)Q}{C V} \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

The value of k' is identical, except for the factor of 100, to the Digestion Index proposed by Mr. Torpey,[26]

$$\text{Digestion Index} = 100 \frac{\text{Gas produced in digester}}{\text{Residual gas in sludge x detention time}}$$

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25 "Sewage and Industrial Wastes," by N. Sawyer and H. K. Roy, Vol. 27, 1955, p. 1356.
26 Ibid., by W. N. Torpey, Vol. 27, 1955, p. 121.

For the data shown in Fig. 19, Mr. Torpey obtained values of the Digestion Index of 90% to 140% per day. The curve shown in Fig. 11 is for a k' value of 1.0 per day, or a Digestion Index of 100% per day, with an undigestible fraction of 48% of the volatile solids in the feed. This gives reasonable agreement with the data for the pilot plant and the treatment plant reported by Mr. Torpey[26] and also the data of Sawyer and Grumbling.

The results for primary sludge obtained by Messrs. Sawyer and Roy[25] indicate a rate constant of 0.84 per day on the assumption of continuous feeding. A somewhat lower rate constant, about 0.7, would produce the same degree of digestion with once a day feeding as was practiced in the experiments.

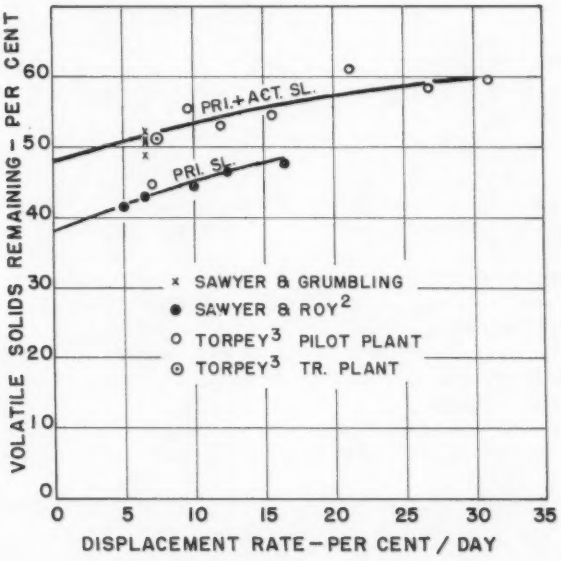

FIG. 11.—EFFECT OF DISPLACEMENT RATE ON VOLATILE SOLIDS REMAINING

The higher rate constant obtained with the activated sludge could be due to the great population of facultative bacteria in the activated sludge. Surely the fact that much of the digestible organic matter has been consumed in forming the activated sludge contributes to the higher undigestible fraction.

The data shown in Fig. 11 indicate good agreement with the first order reaction rate, Eq. 1a, so that for most practical purposes it can be considered to be valid. Because the undigestible fraction must be determined in order to use Eqs. 2, 3, and 5, there seems to be little advantage over the simpler approximation in Eq. 6b and the plot in Fig. 11 because the slope of the line is independent of the intercept or undigestible fraction for a given reaction rate k'.

The effect of the concentration of bacteria bears further consideration. The principal unknown is, of course, the concentration of bacteria. The population is composed of (1) those bacteria introduced with feed, and (2) those produced by growth on the organic matter within the digester. The quantity

produced from the latter source are, in general, proportional to the quantity of organic matter destroyed, so that,

$$(\text{Bacteria}) = B(C_o - C) \quad \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

If this is the principal source, then substitution in Eq. 1a gives

$$\frac{-dC}{dt} = k\,C\,B(C_o - C) \quad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

For a continuously fed digester the equation is

$$Q(C_o - C) = K\,C\,B(C_o - C)V \quad \ldots\ldots\ldots\ldots (10)$$

from which,

$$C = \frac{Q}{k\,B\,V} \quad \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

Combining the constant B with k for a new rate constant k" gives,

$$C = \frac{Q}{k''\,V} \quad \ldots\ldots\ldots\ldots\ldots\ldots (12)$$

This equation states that the concentration of digestible volatile solids remaining is directly proportional to the displacement rate, and independent of the concentration of volatile solids in the feed. This is in contradiction to the conclusions of Messrs. Sawyer and Grumbling based upon their studies, and the report of Messrs. Sawyer and Schmidt,[27] in which it was found that a given detention time produced substantially the same destruction of organic matter. Moreover, there was no pronounced trend to the variations in the data towards an increased destruction of volatiles at the higher sludge concentrations as would be predicted by Eq. 12. In order to look closer at the matter it is necessary to consider the large proportion of undigestible volatiles that it was necessary to assign to the sludge in order to obtain agreement with the first order equation, Eq. 1b.

Writing Eq. 12 in terms of the volatile solids and the undigestible volatile solids gives

$$C_v - x = \frac{Q}{k''\,V} \quad \ldots\ldots\ldots\ldots\ldots\ldots (13a)$$

Dividing all terms by C_{vo} and transposing gives

$$\frac{C_v}{C_{vo}} = \frac{x}{C_{vo}} + \frac{Q}{C_{vo}\,k''\,V} \quad \ldots\ldots\ldots\ldots (13b)$$

According to Eq. 13b the curves in Fig. 11 should be straight lines with slopes of $1/C_{vo}\,k''$. The data is sufficiently scattered that although there is no immediate confirmation of Eq. 13b, it would appear unwise to conclude that the data disprove it.

There are ample reasons for considering that the concentration of bacteria present is significant, the condition that leads to Eqs. 12 and 13b. First, the importance of seeding is well established. Second, the flow scheme of the activated sludge process has been applied to anaerobic digestion of industrial wastes[28] in order to accelerate the digestion by increasing the ratio of bac-

[27] C. N. Sawyer and H. Schmidt, Journal of the Boston Society of Civil Engineers, Vol. 42, 1955, p. 1.

[28] "Biological Treatment of Sewage and Industrial Waste," by A. J. Steffen, Reinhold Pub. Corp., New York, N. Y., 1958, Chapters 1-12.

teria to digestible solids. If Eq. 12 is valid, the value of k" should be applicable to both high rate sludge digestion and other anaerobic digestion processes.

The lack of confirmation of Eq. 12 by the data in Fig. 11 may be due to the increased concentration of inhibiting substances formed when higher concentrations of sludge are digested. The authors found that the gas production decreased with increasing solids concentration in the sludge in the range of 4% to 10% solids. They considered both the reason stated previously and the possibility of loss of gas producing material in the concentration process. The reason is not clear, but they have shown that because of this and the mechanical difficulties of mixing the heavier sludges, concentrations above 6% solids, even with normal ash contents, should be used with caution.

So far the digestion process has been discussed from the standpoint of a single step process, and the agreement of the data with mathematical interpretations has been reasonable. However, it is well known that the process consists of at least two steps; the hydrolysis of complex organic matter to "volatile acids" and the metabolism of the volatile acids to methane and carbon dioxide by the methane bacteria. Under normal conditions the hydrolysis must be the rate controlling step since the concentration of remaining digestible solids is greatly in excess of the volatile acids concentration. Evidence of this can be noted from the data of Messrs. Sawyer and Roy.[25] The volatile solids in the feed sludge was 3.29%, of which 38% was undigestible according to Fig. 11, for an undigestible concentration of 1.25%. At the ten day detention time the digested sludge contained 2.99% solids at 56.4% volatile for a volatile solids concentration of 1.69%. This leaves a concentration of digestible volatiles of 1.69 - 1.25 or 0.44%. This is 4,400 mg per liter as compared to volatile acids of 110 mg per liter. Yet, if the metabolism of the methane bacteria is inhibited, the volatile acids accumulate and failure is immanent. In addition, if the rate of displacement of solids from the process exceeds the rate of growth of the methane bacteria, the process must fail.

So little basic research has been performed on the kinetics of the growth of the methane bacteria that even the maximum rate of growth must be inferred from sludge digestion studies. In a high rate digester the rate of growth (not maximum rate of growth) is equal to the rate of displacement, Q/V. It is obvious that the maximum rate of growth is at least slightly in excess of the greatest displacement rate at which stable operation can be obtained. On the basis of the studies by Mr. Torpey[26] the maximum rate is at least 0.31 per day. E. A. Cassell, A. M. ASCE and C. N. Sawyer have presented[29] evidence that at least two types of methane bacteria are significant. The one that developed last, presumably having the lower growth rate, was responsible for grease destruction and the metabolism the major portion of the volatile acids. However, no attempt was made to determine, from their data, the rate of growth of either group. Until sufficient information is obtained on the maximum rate of growth of the various methane bacteria and the conditions under which these rates obtain, the cause of failure at some particular high rate displacement cannot be ascribed with certainty to the maximum growth rate of the methane bacteria in preference to some unfavorable environmental condition.

Although sludge digestion is a biological process, the problems are so similar to problems of catalysis that it seems pertinent to call attention to

29 "Sewage and Industrial Wastes," by E. A. Cassell and C. N. Sawyer, Vol. 31, 123, 1959.

C. N. Hinshelwood's[30] statement that: "There is no theory of catalysis. The only question is whether we understand catalytic phenomenon well enough to arrange them into a picture of which we like the pattern." Until sufficient information is obtained to formulate a sound theory, there will remain considerable room for personal preference of the various pictures of sludge digestion data that can be arranged.

30 "Journal of the Chemical Society," by C. N. Hinshelwood, 1939, London, England, p. 1203.

OXYGEN BALANCE OF AN ESTUARY[a]

Discussion by Robert V. Thomann, M. B. McPherson, and C. H. J. Hull

ROBERT V. THOMANN,[28] A. M., ASCE.—The author is to be congratulated for a sincere attempt at describing theoretically the complex mechanisms underlying the dissolved oxygen distribution in an estuary. However, there are several areas in the development which require further clarification.

The development assumes non-stratification in both the lateral and vertical directions. As additional data is being collected in different estuaries along the east coast, the assumption of non-stratification may prove to be a poor one. Extreme caution must be used in assuming non-stratified conditions on the basis of limited data. Indeed, the very definition of "non-stratified" should be made more clear since the author implicitly assumes some degree of lateral stratification by using the "probable error" of the cross section results. This degree of stratification is approximately 0.7 ppm of dissolved oxygen as determined from Fig. 4.

There appears to be some confusion with regard to Fig. 1(b) and 1(c). For both the Delaware and James Rivers which are characterized by a progressive wave, the movement of the dissolved oxygen profile during a tidal cycle is determined primarily by the variation in tidal currents. For the two rivers under consideration, flood slack current occurs about 2-3 hr after high water. If Fig. 1(b) and 1(c) are meant to be an illustration of the Delaware and James Rivers, they are somewhat misleading. Fig. 1(c) should show minimum dissolved oxygen at approximately the time the stage height curve is crossing the zero axis.

Mr. O'Connor's approach appears to break down into the following steps:

(a) The determination of a suitable fresh water inflow rate to arrive at the forward velocity, U,

(b) the graphical determination of the eddy diffusion term, ϵ, using the U obtained from (a) and suitable field data,

(c) the graphical determination of the coefficient, j_1,

(d) the solving for K_d using (a), (b), and (c) and Eq. 5,

(e) the determination of the reaeration coefficient, K_2, from suitable field data,

(f) the solving for the coefficient, j_2 using (a), (b), and (e) and Eq. 10,

(g) solving for the quantity F by means of Eq. 9, and

(h) the solution of Eq. 7 using j_1, j_2, F, and field data.

The author fails to make clear the mechanism used to arrive at the forward velocity needed. For the Delaware, it is not clear whether the flow on the same

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[a] May, 1960, by Donald J. O'Connor.

[28] Sr. Asst. San. Engr., U. S. Public Health Service, New York Univ., Dept. of Meteorology and Oceanography, New York, N. Y.

day of sampling was used or whether some lag period was allowed. Recent model studies conducted by the Corps of Engineers at the Delaware model in Vicksburg, Mississippi for the Interstate Commission on the Delaware River and the City of Philadelphia, have indicated that the time of travel of the centroid of mass of a dye release at Trenton, New Jersey to the stretch of the Delaware under consideration might vary from about 10 days for the higher flows to as much as 30 - 90 days for the lower flows. The determination of the rate of fresh water inflow to be used in the application of this approach is critical and an extremely difficult one, the procedure of which should be indicated. As is discussed subsequently, the development allows for considerable latitude in this regard, thereby indicating the possible insensivity of the approach to the magnitude of the fresh water inflow.

Step (b) requires suitable data of a conservative variable existing in the estuary in sufficient quantities to be measured with present techniques. It is fortuitous that the stretch of the Delaware under consideration afforded this variable in terms of the chloride content. However, in the upper end of the Delaware estuary, it is not believed that such a consituent exists.

Regarding the graphical approach used in determining the eddy diffusion term, the basic data for the chloride content measured during the November 13, 1956 series (Fig. 4) was given to another individual unfamiliar with this field but familiar with approximating a straight line to a set of points by eye. This individual obtained an ϵ of 9.2 exactly the same as the author's for the October 9, 1956 series (Fig. 4). Again, the approach does not appear to be sensitive enough to distinguish the difference between these values.

The graphical determination of the coefficient j_1 is subject to the same errors although in this case the prior mentioned individual did somewhat better estimating a j_1 of about -0.04 as compared with -0.047 computed from the data contained in the paper.

The remaining steps of the development are fairly straightforward assuming one is willing to accept the application of Eq. 20 to estuaries and Eq. 21 to the reaeration coefficient. It would have been helpful if the author had indicated the survey of the Delaware for which an "adjustment" of the K_2 value was made and at least generally, the nature of the adjustment.

It is important to note that suitable field data must be available to determine c_0 and c_s. If one were placed in the position of using this development to predict, for example, the effect of increasing the pollutional load to the stream, these quantities would have to be assumed.

The writer using the data from the November 13, 1956 series duplicated the procedure outlined using, however, the eddy diffusivity of 9.2 indicated above and the U of 0.82 used in the October 9, 1956 series. In view of the transit time from Trenton, New Jersey to the area under consideration, this latter quantity can be reasonably justified. The use of these values yielded a dissolved oxygen profile almost exactly similar to the November 13th series indicated in Fig. 4. Hence, the use of a flow rate of 7,450 cfs instead of 11,600 cfs and a turbulent transport coefficient of 9.2 instead of 10.8 resulted in a similar profile. Both the flow rate of 7,450 cfs and an ϵ of 9.2 could have logically been chosen to determine the final profile. One wonders then, whether the development actually is able to distinguish definitive cause and effect relationships.

M. B. McPherson,[29] M. ASCE.—This discussion is addressed to the hydraulic aspects of the paper. In particular, the procedure employed in arriving at

[29] Prof. of Hydr. Engrg., Dept. of Civ. Engrg., Univ. of Illinois, Urbana, Ill.

a constant diffusion coefficient will be examined and the absence of an adequate theory describing the time-distribution of fresh water inflow will be recognized. Only the Delaware River situation will be considered.

In a recent discussion,[30] various contemporary non-conservative pollution studies of the Delaware River were briefly described. The following paragraph from the discussion is directed to the author's paper:

> "After (Kent's) paper was published, O'Connor compared calculated with observed dissolved oxygen profiles for one HWS (high water slack) and two LWS (low water slack) boat sampling runs made in the latter half of 1956 by the State of Delaware Water Pollution Commission. The profiles used were for the rising end of the curves beyond the minimum concentrations, for five stampling points extending from Station +193 to Station +305. Since the data was collected at the "same slack" and the river flow was "low," it was assumed conditions were steady and diffusion coefficients were calculated from the observed chloride profiles. In addition, it was assumed that the diffusion coefficient, the channel cross section and the mean transport velocity were constant over the reach studied. O'Connor suggests that the distribution of a stable dissolved chemical ion might be utilized as a spacial tracer for the section of the river upstream from the salinity front. Since there are no significantly distributed spacial tracers extant in most of the non-saline section, a special tracer would have to be introduced prior to sampling. Although O'Connor cites fresh-water inflow rates, they are not necessarily the true rates which contributed to mixing and transport."

TABLE 2.—STATION RELATIONS, DELAWARE RIVER

Location	Fig. 4, O'Connor, approximate miles	State of Delaware Water pollution Commission, miles	C. of E. (and Kent), approximate, 1000's of feet
(1)	(2)	(3)	(4)
Smyrna River	24.8	0.00[a]	+305
Appoquinimink Creek	19.5	5.30[a]	+277
Reedy Island	15.5	9.28[a]	+256
Pea Patch Island	9.4	15.38[a]	+224
New Castle	3.6	21.18[a]	+193
Cherry Island	. . .	26.00[a]	+168
State Line	. . .	33.69[a]	+127
Allegheny avenue (Phila.)	. . .	57.52	0 + 0
Trenton (head of tide)	. . .	87.51	-160

[a] Stations at which samples were taken on the three 1956 Surveys partially used by O'Connor.

Because model data will be introduced, the approximate relations between the stationing used in the paper, by the State of Delaware Water Pollution Commission[22] and by the Waterways Experiment Station, are given in Table 2. The

[30] Discussion of "Diffusion in a Sectionally Homogeneous Estuary," by M. B. McPherson, Proceedings, ASCE, Vol. 86, No. SA 5, September, 1960.

chloride data for the three Delaware River surveys are listed in Table 3 and plotted in Fig. 7. Only one of the three chloride profiles has been graphed in the paper, Fig. 3(a), Survey of October 9, 1956. Data for two of the seven locations occupied in each survey were excluded by the author. Inasmuch as wastes discharged into the upper river contribute chlorides to the low-concentrations at the upstream end of the profile, it would be reasonable to ignore data for very low concentrations. However, the author's reason for using only the data for concentrations above, about 200 ppm (as opposed to say 50 ppm), is not clear. The divergence of the upstream data points from an approximate constant exponential (straight line) relation does not appear to be the basis for their exclusion, because the two profiles not shown by the author do not satisfy very well the condition of constant velocity and eddy coefficient as used in his application of Eq. 16. Since any interpretation would be quite arbitrary, it is requested that the author cite the values of eddy coefficient used in his calculations.

TABLE 3.—CHLORIDE DATA FOR 1956 DELAWARE RIVER SURVEYS,[a] SURFACE, SHIP CHANNEL

State of Delaware W.P.C., Miles	Station From Philadelphia Approximate	CHLORIDES, in ppm		
		Aug. 23, 1956	Oct. 9, 1956	Nov. 13, 1956
0	+305	4,857	5,250	6,900
5.3	+277	3,733	3,400	4,500
9.28	+256	2,340	2,470	2,850
15.38	+224	1,270	1,420	1,300
21.18	+193	603	810	320
26.00	+168	177	273	75
33.69	+127	60	58	18
Current		LWS	LWS	HWS
"Trenton Flow," in cfs		5,130	5,540	6,500
Q, O'Connor, Table 1, in cfs		(5,300)	(7,450)	(11,600)
Trenton Flow, USGS, Date of Survey, in cfs		(4,630)	(5,140)	(6,100)

[a] "Investigation of Sanitary Water Quality in the Lower Delaware River," by A. J. Kaplovsky, Tech. Report II, Water Pollution Comm., State of Del., December, 1956.

The phrase "probable error from statistical analysis of cross sectional data" appears as a footnote in Fig. 3. It would be highly appropriate for the author to state the statistical significance of the ranges plotted in the several figures. Because the various constants were somewhat arbitrarily assigned, a question immediately arises as to what the effect would have been on the computed oxygen profiles had other values been selected because the good agreement may have been achieved by serendipity. The statement in the Synopsis, "The assumption of constant coefficients in the equation is confirmed by the field data . . . ," presumably was not intended to include the eddy coefficient for the Delaware River.

The State of Delaware Water Pollution Commission, in cooperation with Incodel, has made twenty-three "same slack" runs in the June through October period of the intervening three years, 1957-1959. Of these, eighteen were at LWS and five at HWS, with two of the twenty-three on the same day. All of

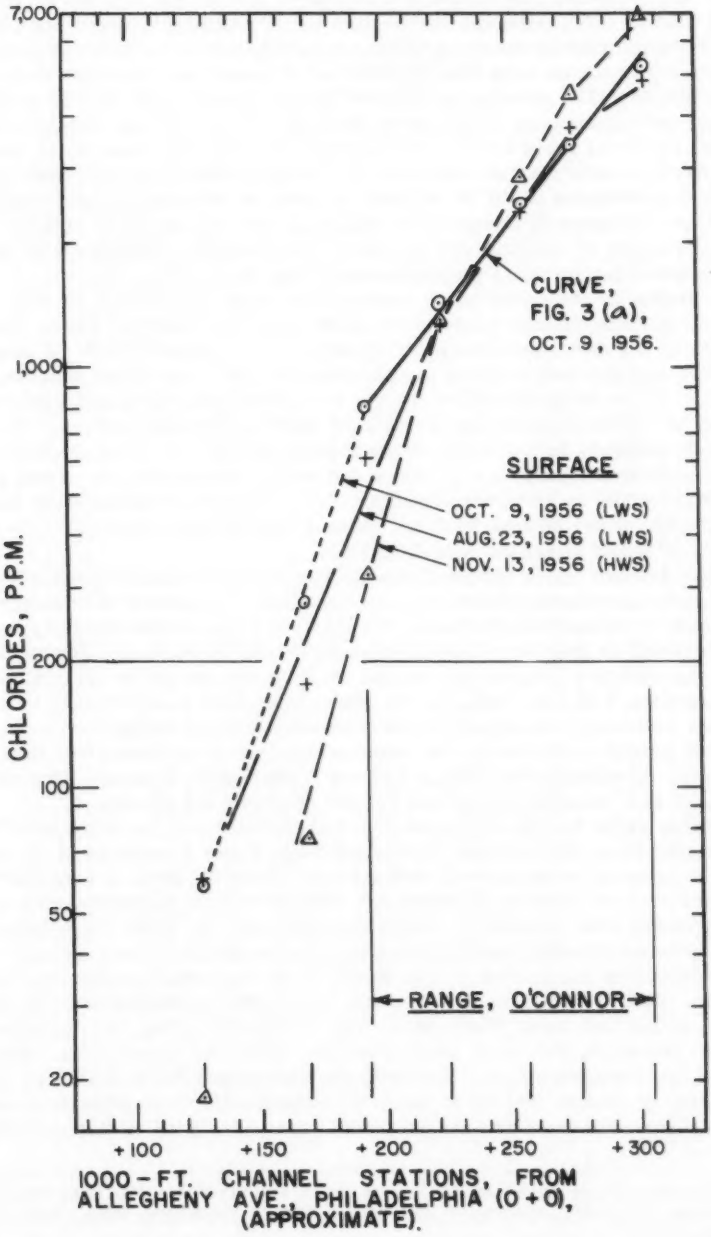

FIG. 7.—SALINITY PROFILES FOR DELAWARE RIVER SURVEYS OF FIG. 4.

these runs extended from Fieldsboro at about Station -127 to Reedy Island at about Station +256, covering the section of the estuary of major oxygen concentration interest by means of fifteen sampling locations. The minimum D. O. for the twenty-three runs was observed at or upstream from the State Line, about Station +127. However, a chloride concentration equal to or greater than 50 ppm extended only as far as about Stations +100 to +130 for the HWS observations and from about 0+0 to +190 for the LWS. The minimum D. O. was thus well above the principal salinity front for many of the runs. In order that the author's procedures could be utilized to compute complete oxygen profiles, it would be necessary to integrate an instantaneous release or to employ a continuous release of tracer above the reach to be sampled. This has been implied in the quoted paragraph in the beginning of this discussion.

Returning to the question of constancy of eddy coefficient, in Fig. 8 are graphed surface salinity profiles obtained from the Delaware River model at Vicksburg for sustained, steady, fresh water inflow schedules.[31] A semilogarithmic straight line relation is approximated only over short reaches. The unsteady inflow in the prototype results in chloride profiles which might be regarded as traces intersecting several of these or similar curves. The continuously unsteady inflow might cause a more straight or more diverse semilogarithmic distribution than indicated for steady flow conditions. Thus, a constant exponential relation would obtain over a short reach infrequently and unpredictably. Other effects, such as seasonal and storm, stage and tide range changes,[32] would affect the salinity profile.

There are two major facets of the Delaware River pollution problem which are attended by considerable economic liabilities. A number of attempts have been made to relate B. O. D. loadings and inflow rates to observed oxygen levels. Seasonal or long term loading changes do not necessarily have any bearing on the author's procedures, except an extended series of calculations be compared one with the other. On the other hand, flow rates thought to be associated with observed oxygen levels have been and are being used to project expected future oxygen levels for various amounts of proposed low flow augmentation. In addition, the author's use of a seemingly arbitrary flow rate to determine the "velocity due to land runoff" requires examination.

The flow rates for the Delaware River at Trenton and the Schuylkill River at Fairmont Dam, Philadelphia, are tabulated in Table 4 in terms of the number of days prior to the date of each survey. These U. S. G. S. data are "Unpublished records, subject to revision." The main stem and tributaries to the estuary suffer little natural or controlled regulation. In Table 5 are listed the inflow rates employed in model studies to simulate the long-term means.[9] The rates identifying the curves of Fig. 8 are all for the total contribution above about Sta. +60. The maximum rate used, 16,475 cfs, corresponds to the long-term mean for that point, Table M-4. The 16,475 cfs at Sta. +60 includes the flow at Trenton, at Fairmont Dam, from the Rancocas Creek (Sta. -40) and Philadelphia sewage treatment plant effluent discharged below Fairmont Dam. An average of almost 300 cfs is taken by Philadelphia from Schuylkill water supply intakes situated above the Fairmont gage; nearly all of this quantity is

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31 "Delaware River Model Study, Report No. 2, Salinity Tests of Existing Channel," Tech. Memo. No. 2-337, Waterways Experiment Station, Vicksburg, Miss., June, 1954, Plates 13-18.

32 "Salinity of the Delaware Estuary," by Bernard Cohen, U.S. Geological Survey Open File Report, Philadelphia, Penna., July, 1957.

TABLE 4.—COMBINED FLOWS FOR DELAWARE RIVER AT TRENTON AND SCHUYLKILL RIVER AT FAIRMONT DAM.[a]

Number of days prior to date of Survey	Date of Sampling Survey: Aug. 23, 1956 — Flow at trenton gage, Delaware River, in cfs	Aug. 23, 1956 — Flow at Fairmont Dam, Philadelphia, Schuylkill River in cfs	Aug. 23, 1956 — Total flow, not including Rancocas Creek, in cfs	Oct. 9, 1956 — Flow at trenton gage, Delaware River, in cfs	Oct. 9, 1956 — Flow at Fairmont dam, Philadelphia, Schuylkill River in cfs	Oct. 9, 1956 — Total flow, not including Rancocas Creek, in cfs	Nov. 13, 1956 — Flow at trenton gage, Delaware River, in cfs	Nov. 13, 1956 — Flow at Fairmont Dam, Philadelphia, Schuylkill River in cfs	Nov. 13, 1956 — Total flow, not including Rancocas Creek, in cfs
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
0	4,630	1,290	5,920	5,140	929	6,069	6,100	1,910	8,010
1	4,740	1,910	6,650	5,420	1,200	6,620	6,700	2,050	8,750
2	3,900	1,270	5,170	4,700	1,120	5,820	7,350	2,290	9,640
3	3,500	410	3,910	4,630	892	5,522	7,600	2,590	10,190
4	3,530	430	3,960	4,420	892	5,312	7,950	2,830	10,780
5	3,620	470	4,090	4,420	855	5,275	8,650	3,240	11,890
6	3,680	510	4,190	4,630	818	5,448	9,500	3,820	13,320
7	3,860	670	4,530	4,980	892	5,872	10,700	4,500	15,200
8	4,000	670	4,670	5,300	966	6,266	13,000	5,800	18,800
9	3,720	606	4,326	5,860	1,080	6,940	14,100	7,700	21,800
10	3,760	606	4,366	6,550	1,120	7,670	13,300	13,000	26,300
11	3,860	744	4,604	7,120	1,290	8,410	12,200	7,700	19,900
12	4,100	744	4,844	8,950	1,000	9,950	7,120	2,100	9,220
13	4,280	892	5,172	7,840	1,200	9,040	5,740	1,500	7,240
14	4,520	1,080	5,600	5,500	1,200	6,700	5,700	1,770	7,470
15	4,820	1,388	6,208	5,540	1,050	6,590	5,820	2,150	7,970
16	4,600	1,388	5,988	6,180	920	7,100	6,140	2,390	8,530
17	4,520	1,290	5,810	5,100	980	6,080	6,700	2,680	9,380
18	4,490	929	5,419	5,700	910	6,610	7,800	3,290	11,090
19	4,630	781	5,411	6,550	980	7,530	9,200	4,800	14,000
20	4,780	818	5,598	5,540	1,040	6,580	10,100	6,070	16,170
21	4,980	855	5,835	4,600	1,200	5,800	4,920	1,770	6,690
22	5,100	966	6,066	4,490	1,450	5,940	3,900	574	4,474
23	5,340	1,120	6,460	4,100	1,100	5,200	3,930	542	4,472
24	5,980	1,370	7,350	4,000	1,030	5,030	4,000	542	4,542
25	6,920	1,630	8,550	4,100	1,100	5,200	4,040	638	4,678
26	6,960	1,580	8,540	4,280	1,200	5,480	4,140	638	4,778
27	6,500	1,290	7,790	4,520	1,350	5,870	4,100	638	4,738
28	7,120	1,500	8,620	4,740	1,500	6,240	4,000	707	4,707
29	7,950	1,860	9,810	5,660	1,860	7,520	3,960	670	4,630
Average 10 days	3,918	824	4,742	4,950	964	5,914	9,165	3,673	12,838
Average 20 days	4,138	904	5,042	5,726	1,015	6,741	8,569	3,905	12,474
Average 30 days	4,813	1,036	5,849	5,352	1,104	6,456	7,282	3,030	10,312

[a] Not including flow from Rancocas Creek, surveys of Fig. 4 and Table 1.

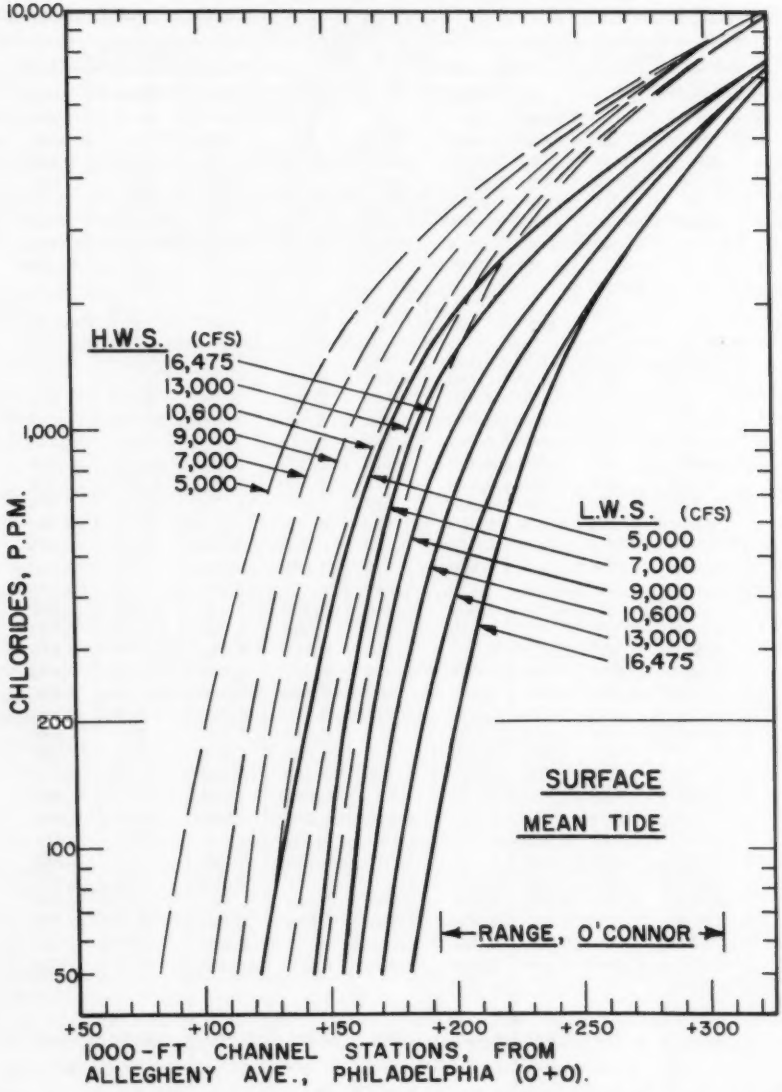

FIG. 8.—SALINITY PROFILES FOR VARIOUS RATES OF STEADY FRESH WATER INFLOW—AT AND INCLUDING THE SCHUYLKILL RIVER

returned below the dam. As may be found from Table 5, the long-term mean contribution from the Rancocas is estimated at 875 cfs, but only the N. Branch at Pemberton, N. J. is gaged, which accounts for only about one-fifth of the true total Rancocas flow. The long-term mean from the mouth of the Schuylkill for Table M-4 is 3,250 cfs. At about Sta. +170 the long-term mean contribution from the Christina R. in Delaware is taken at 1,100 cfs, with 450 cfs from the Salem R. in N. J. at about Sta. +235. All of the above fresh water sources contribute to the reach between Stations +193 and +305, utilized by the author.

In Table 4 the daily flows at Trenton and Fairmont Dam for the same calendar day have been added together. This was done for illustrative purposes only, as the former is over forty river miles upstream from the latter and hydrograph variations are far from synchronised at any time. Also given are the corresponding 10-day, 20-day and 30-day averages for periods prior to an including the date of survey, for comparison. At the bottom of Table 3 are listed the flows given elsewhere[22] and those in Table 2. How did the author arrive at the figures used? Was the flow for the Delaware surveys indeed "low?"

TABLE 5.—LONG TERM MEANS, TOTAL FRESH WATER INFLOW AT VARIOUS STATIONS USED IN MODEL STUDIES, DELAWARE RIVER ESTUARY

Approximate Station (1)	Total fresh water flow, in cfs (2)
-160 (Trenton)	12,350
- 40	13,225
+ 60	16,475
+170	17,575
+235	18,025
+340	18,400
+420 (To Capes)	20,200
Range, O'Connor, Approximately Stations +193 to +305	

The author states that: "The basic relationships defining the processes of deoxygenation and reaeration in rivers must be related to the flushing times in order to define the oxygen balance in an estuary." It is not clear whether or not flushing times were a consideration in the author's calculations. If the approximate time observed for the movement of the centroid of a dye profile in the model under steady flow conditions may be used as an index of travel time for fresh water inflow,[30] a flow at Trenton of 12,350 cfs (schedule of Table 5) would take about 21 days at LWS and 27 days at HWS to travel from Trenton to Sta. +193. With 5,000 cfs at Trenton the travel time would be about 52 days at LWS and 66 days at HWS. With these approximations in mind and considering that only thirty days are represented in Table 4, one is inclined to question seriously the premise: "A steady state condition is assumed to exist which implies that the land runoff and the waste discharge have remained constant for a period equivalent to the time of passage through the estuary."

While the reader is entitled to some explanation as to the meaning of "land runoff" and the procedures used in arriving at the figures cited, the author obviously and unquestionably is not responsible for the absence of an adequate theory or rationale for appraising inflow, particularly where extrapolation to

presumed low flow augmentation conditions is an issue. However, the value of all attempts to analyze estuarine oxygen balances will be extremely limited until such time as the contributing effects from inflow can be separated. The complexity of gaging directly the flow of a tidal stream may be appreciated from the following example: In the vicinity of Sta. +127 the total long-term mean fresh water inflow is as large as only about 8% of either the total mean flood discharge or the total mean ebb discharge;[33] the critical drought flows are obviously so small as to be inseparable. A time-synchronized integration of fresh water inflow sources, using steady state transit times obtained from the model, requires the imposition of a conceptual mechanism for the natural unsteady state, along with seriously restrictive boundary conditions. Perhaps the most logical and feasible approach would be by means of the existing hydraulic model, to test the appropriateness of the several bases through which

TABLE 6.—DATA FOR 1956 DELAWARE RIVER SURVEYS,[a] SURFACE, SHIP CHANNEL[b]

Stations From Philadelphia, Approximate, 1000's of feet	Aug. 23, 1956			Oct. 9, 1956			Nov. 13, 1956		
	Temperature, in °C	D. O. Sat., in %	(5-Day) B.O.D., in ppm	Temperature, in °C	D. O. Sat., in %	(5-Day) B.O.D., in ppm	Temperature, in °C	D. O. Sat., in %	(5-Day) B.O.D., in ppm
+305	25.0	85.0	3.07	17	80.8	2.4	12.0	88.0	4.2
+277	25.0	91.7	2.47	17	77.7	1.67	12.0	83.0	7.4
+256	25.0	83.3	1.60	17	72.2	2.4	12.0	81.0	4.6
+224	25.5	68.4	1.20	17	56.5	4.2	12.0	68.4	5.2
+193	25.5	48.3	2.50	17.5	41.8	7.6	12.0	48.3	10.8
+168	26.0	38.7	0.70	18	33.8	9.6	13.0	42.0	15.6
+127	26.0	43.3	6.13	18	29.4	13.8	13.0	38.5	3.0

[a] "Investigation of Sanitary Water Quality in the Lower Delaware River," by A. J. Kaplovsky, Tech. Report II, Water Pollution Comm., State of Del., December, 1956.
[b] Chlorides listed in Table 3.

the unsteady case might be analyzed. It is the writer's firm opinion that oxygen balance analysis will not reach the degree of precision and adequacy urgently needed until the true contribution, large or small, of fresh water inflow can be appraised.

The published data[22] for the Delaware River surveys is given in Table C. Only the October 9, 1956 B. O. D. data were presented by the author, Fig. 3(b). The B. O. D. data for the other two surveys are more divergent.

The report of the Public Health Service seminar of 1958[34] properly could have been added to the generous bibliography in the paper. An important ref-

[33] "The Prototype and Model Delaware Estuary," by C. F. Wicker, Proceedings, 6th Genl, Meeting Internatl., Assoc. of Hyd. Res., A 12-1, The Hague, The Netherlands, 1955, (Table VIII).
[34] "Oxygen Relationships in Streams," a Seminar, The Taft Sanitary Engrg. Center, Technical Report W58-2, Cincinnati, Ohio, March, 1958.

erence on the regression analysis approach has recently been brought to the writer's attention.[35]

C. H. J. Hull,[36] M. ASCE has presented a simplified technique for determining the self-purification of fresh water streams in which the need for determining coefficients of deoxygenation and reaeration or time of flow is eliminated. It is possible that this technique may be adaptable to estuarine analyses using data for the same tidal phase. Temperature, D.O. and B.O.D. are the only measurements required.

C. H. J. HULL,[37] M. ASCE.—Mr. O'Connor has presented a theoretical analysis purporting to define the processes which determine the distribution of dissolved oxygen in a non-stratified estuary. The author merits praise and encouragement in his efforts to unravel the extremely complex relationships involving the use, replenishment, and movement of oxygen in tidal waters. The reasonably good correlations between the computed and observed DO profiles for the Delaware and James Rivers tend to support the use of the formulations presented for purposes of determining treatment requirements of wastes to be discharged into such waters. The correlations also tend to justify using Mr. O'Connor's relationships for determining the minimum freshwater flow requirements into estuaries such as the Delaware in which the land runoff is regulated by diversions and storage projects.

On the other hand, studies and experience by this writer lead him to question the validity of certain assumptions implicit in the author's analysis if his method is to be applied generally to any non-stratified estuary for any season or time of day. These assumptions are: (a) that the temperature dependency of the deoxygenation coefficient is truly as shown by the relationship (Eq. 21) found empirically by H. W. Streeter and E. B. Phelps (53)[38] in their Ohio River studies; and (b) that the only means of replenishing the oxygen used in the stabilization of organic matter is by the transfer of atmospheric oxygen across the air-water interface.

In view of the long standing and wide acceptance of these two assumptions among sanitary engineers, it requires some audacity to question them. As Benjamin Franklin (9) put it two hundred years ago,

> "'Tis a kind of audacity to call such general opinions in question, and may call one to censure. But we must hazard something in what we think the cause of truth: and if we propose our objections modestly we shall tho' mistaken, deserve a censure less severe, than when we are both mistaken and insolent . . ."

(Coincidentally, this quotation was from Franklin's discussion of the movement, or lack of movement, of fresh water through an estuary to the sea. As a matter of historical interest, the entire discussion is recommended to those interested in estuarine hydrology).

Actually, considerable evidence is readily available to show that the first assumption is not strictly correct. As for the second, the published scientific

35 "A Three Cycle Analysis of Water Quality Variables in Tidal Estuaries," by R. V. Thomann, A. N. Diachishin, P. DeFalco, Jr., and L. M. Klashman, AAAS International Oceanographic Congress, Preprints, Washington, 31 August-12 September, 1959, p. 709.

36 "Report No. 111 of the Low-Flow Augmentation Project," by C. H. J. Hull, The Johns Hopkins University, Baltimore, Md., April, 1960.

37 Research Associate, Dept. of San. Engrg. and Water Resources, The Johns Hopkins Univ., Baltimore, Md.

38 Numerals in parentheses, thus (53), refer to corresponding items in the Reference section located at the end of the discussion.

literature is replete with evidence to the contrary, so much of it that it becomes difficult to overlook or ignore. It should help to examine briefly the evidence on both the temperature dependency of the deoxygenation coefficient and the sources of oxygen found dissolved in natural surface waters.

Temperature.—Recently, in connection with an investigation of low-flow augmentation for pollution abatement, the writer found it impossible to obtain agreement between DO profiles observed in a stream in winter and those predicted by transposing the deoxygenation coefficient determined in summer to winter temperatures by means of the temperature-correction formula cited by the author (Eq. 21). This led to a review of the technical literature on the effects of temperature on BOD rates, as reported by Hull and Carbaugh (21). Briefly, the review indicated that the formulation, Eq. 21, derived by Messrs. Streeter and Phelps (53) and purportedly confirmed by E. J. Theriault (54) is not adequately supported by experimental data. The thermal-correction coefficient, θ, in the relationship

$$K_{T'} = K_T \, \theta^{T' - T} \quad \ldots\ldots\ldots\ldots\ldots\ldots (22)$$

is apparently not really a constant with the value of 1.047, as hypothesized by those early investigators. Examination of their data along with those of E. W. Moore (29) and H. B. Gotaas (13) strongly suggests that θ itself is a continuously varying function of temperature. The coefficient, θ, appears to vary non-linearly, decreasing from about 1.15 for temperatures near the freezing point to about 0.97 for temperatures near 35°C. Fortunately, the curve of θ versus temperature passes through the value of 1.047 in the range of summer temperatures normal for most surface waters. This justifies use of Eq. 22 with a θ value of 1.047 for approximating temperature corrections over the summer range from about 18°C to 27°C, although the refinement indicated by three decimal places is hardly supported by available data. However, for regulated streams where winter temperatures are involved, or in streams heated to 30°C or higher by thermal pollution, the use of the Streeter-Phelps temperature-correction coefficient of 1.047 does not appear to be justified. Therefore, in these situations, Eq. 21 must be used with caution. It would be possible, of course, to determine the deoxygenation coefficient empirically at the desired temperature by carrying out the necessary field work in the time of year concerned, thus eliminating the need to transpose the coefficient by the use of Eq. 21.

The writer does not intend to imply that until now the value of 1.047 for θ has been universally accepted without question. Earlier writers, in addition to Messrs. Moore and Gotaas, already cited, have mentioned the doubtful nature of the knowledge of temperature effects on self-purification. M. LeBosquet, Jr. and E. C. Tsivoglou (27) pointed out the need for more exhaustive investigation of temperature-correction coefficients. W. M. Ingram and W. W. Towne (22), in discussing the effects of the heating of natural waters by industrial wastes, noted that the influence of such heating on the metabolic processes of biota as reflected in measurements of oxygen demand is not fully understood, although long recognized. In spite of these and other cautioning statements which have appeared, and the available evidence to the contrary, Eq. 21 and the thermal-correction coefficient of 1.047 continue to be used for engineering purposes. While the lack of a better method of determining temperature effects tends to justify and necessitate using Eq. 21 at present, the weakness of the support for this method calls for further research.

In the meantime, it appears unwise to place unlimited confidence in self-purification computations based on this weak foundation.

Sources of Oxygen.—This writer has previously stressed the fallacy of assuming only the atmosphere as a source of oxygen for waste stabilization (C. H. J. Hull 18, 19). The production of oxygen in natural waters by photosynthesis of phytoplankton and benthic algae is recognized by all limnologists, oceanographers, biologists, and sanitary engineers. However, among these various fields of overlapping interests, the sanitary engineers have been uniquely reluctant to attempt quantitative evaluation of this factor for use in estimating the self-purification capacity of surface waters. Although most engineers writing on this subject have recognized that photosynthesis may be significant as a source of oxygen, they have generally mentioned it only in vague, qualitative, short statements of a sentence or two. They have attempted to justify their lack of attention to photosynthetic oxygen by referring to the difficulty of accurately determining this factor, or by pointing out that it is an undependable source, or that the oxygen produced is subsequently consumed by algal respiration and therefore of no importance.

As for difficulty, quantitative estimation of photosynthesis by the light-and-dark-bottle technique used by Gaardner and Gran (10) in Oslo Fiord, by S. M. Marshall and A. P. Orr (28) in the sea, and by H. A. Schomer and C. Juday (49) in Wisconsin Lakes is probably no more involved than the determination of the coefficient of eddy diffusivity or of the coefficient of atmospheric reaeration (if, indeed, the latter can be determined at all during daylight hours without knowledge of the photosynthetic oxygen-production rates). Newer methods have been proposed, some of which promise to be relatively simple and reasonably accurate (H. T. Odum, 33; J. H. Ryther, 47; J. Verduin, 57).

The argument that photosynthesis is not a dependable source of oxygen for natural streams appears incompatible with the increasing dependence being placed upon photosynthesis in sewage oxidation ponds. These ponds are gaining widespread favor as a means of protecting streams from excessive pollution. In this case, engineers have attempted to measure photosynthesis as a purification factor (W. J. Oswald and H. B. Gotaas, 34) dependable in artificial ponds, there appears to be no reason to believe that photosynthesis is less dependable in natural water bodies.

Even if not dependable in the sense that it is uniformly productive day by day, the statistical significance of photosynthesis is no less than that of variable stream flows, variable waste loads, or variable atmospheric reaeration caused by variable winds and—of all things—by the variation of the dissolved-oxygen deficit attributable to the nondependability of photosynthesis.

If photosynthetic oxygen production rates are only at times significant, then special care must be taken in oxygen-balance studies to avoid the error of crediting these undependable photosynthetic reoxygenation rates to atmospheric reaeration. Unless photosynthesis is taken into account, the reaeration coefficients computed from observed dissolved-oxygen data will automatically include a photosynthetic component. Therefore, if dependability is the criterion for a significant oxygen source worthy of study, the investigator is forced to consider the "undependable" in order to evaluate the "dependable."

As for algal respiration cancelling the benefits of photosynthesis, this appears to be a widespread opinion unsupported by experimental evidence or field observations. The sharp drop in DO concentration following sunset seems

generally to have been attributed largely to algal respiration. Usually unanswered are the questions: (1) What part of this DO drop can be attributed to bacterial respiration? and (2) What part of this DO drop can be attributed to atmospheric deaeration of water supersaturated with DO after exposure to daylight for about twelve hours?

Considerable evidence is available to support the contrary opinion that, in many instances, algal photosynthesis more than balances the algal respiration. D. W. Pritchard (38) has offered the following explanation:

> "There exists a frequent mis-conception that there cannot be a net production by photosynthesis over respiration since the death and decay of the organisms will utilize as much oxygen as was produced in the original fixing of carbon into organic compounds. Actually, a significant portion of the dead organic material sinks to the bottom and is incorporated into the sediments there before it can exert an oxygen demand on the water. The breakdown of this organic material within the sediments takes place very slowly, and by chemical processes which do not utilize free oxygen. Some of the material remains in the organic state without ever being completely oxidized."

Mr. Pritchard's argument is supported by Franz. Ruttner (46) who states that in lakes,

> ". . . the quantity of organic material per unit volume of water destined for decomposition there (hypolimnion) is indeed small in comparison to the accumulations of the same material in the sediments. . . . That these materials are able to outlast even geological epochs is demonstrated to us by sapropelite, by sedimentary bituminous deposits, and not the least by petroleum."

The slow decomposition of algae is supported also by H. W. Harvey (15), who comments that

> ". . . whole algae fall to the bottom, . . . for some odd reason the algae are only very slowly decomposed by bacteria and protozoa, although both unicellular and filamentous algae are extremely rich in protein."

Actually, to be significant in oxygen-balance computations, the oxygen demand of organic matter synthesized by algae need be delayed only a matter of a few hours in some cases. For example, in computing the reoxygenation coefficient for a short stretch of a stream using DO values observed during daylight, the time of flow through the stretch would be measured in hours, or possibly as much as a day. The fixing of carbon in the stretch would be accompanied by oxygen release. Any photosynthetic oxygen remaining in the water at the downstream end of the stretch would affect the reoxygenation coefficient if computed in the usual way. That this influence is significant is shown by the differences between daylight and darkness values of coefficients computed by M. A. Churchill (6), to be discussed subsequently. The significance has also been shown many times, of course, by the persistence for several days of DO gains in bottles exposed to light as opposed to the loss of DO in bottles kept dark in the light-and-dark-bottle technique of measuring primary production.

A. L. H. Gameson (11) recently commented on the significance of photosynthetic oxygen production measurements in the Thames estuary by A. B.

Wheatland (58). Mr. Gameson pointed out that the net effect of photosynthesis depends on the ultimate fate of the decaying planktonic plants:

> ". . . if they are completely oxidized before passing out of the estuary their net effect on the oxygen balance will be slight, but if they fall to the bed of the estuary and are covered up so that oxygen cannot reach them or are removed by dredging, or if they pass out of the estuary in suspension, then the net effect during the year will be a gain in oxygen."

Mr. Gameson did not reach any conclusion concerning the fate of the carbon fixed annually in the Thames. However, it appears to the writer that the annual net effect is of far less significance than the net effect during the shorter period of critical summer conditions observed in most polluted estuaries. If photosynthesis provides a net gain of oxygen during the critical period, it is an asset in the oxygen balance. As already pointed out, moreover, a net gain over a period of a few hours can significantly affect oxygenation and deoxygenation coefficients computed from DO observations. Another way in which algae-synthesized organic carbon is removed from estuaries before decaying and exerting an oxygen demand is by entering the food chain of fin fish and shellfish which are themselves removed by commercial or sports fishermen. This is an item of no small importance in many estuaries.

In reviewing the literature on the oxygen balance of natural waters, this writer has been struck by the two different underlying opinions concerning photosynthetic oxygen production. The first, held largely by the writer's colleagues in the sanitary engineering field, is that photosynthesis is relatively unimportant and can be ignored. The second, adhered to by other groups of water scientists, is that photosynthesis as a significant source of oxygen is a long established fact and must be considered in oxygen-balance studies. Indeed, these latter experts will undoubtedly consider this discussion redundant, and wonder at the need to emphasize the importance of photosynthesis at this late date.

It should be noted that there are exceptions in sanitary engineering literature in which quantitative measurements of photosynthesis have been reported. The writer (Hull, 17), cited by C. F. Garland (12), using the light-and-dark-bottle technique, measured summer photosynthesis in the estuarine waters of Baltimore Harbor, an arm of Chesapeake Bay. The plankton algae were estimated to contribute 23.6 lb of oxygen per acre per day (2.65 g per sq m per day). This was the average production determined from 12 measurements covering the three different stations in the harbor. It is pertinent to note that this amounts to about 600,000 lb per day of photosynthetic oxygen production in the harbor, more than four times the atmospheric oxygen absorbed daily, as estimated by Garland (12). However, as Mr. Garland pointed out, Baltimore Harbor would be capable of greater atmospheric reaeration at greater oxygen deficits. Of course, photosynthesis must be credited with keeping the deficit relatively small.

I. Nusbaum and H. E. Miller (31), also using light and dark bottles, determined photosynthetic oxygen production in San Diego Bay. According to them, biological activity of chlorophyl-bearing plankton accounted for 178,500 lb per day of oxygen. By comparison, they estimated that atmospheric reaeration provided only 132,700 lb per day. These investigators noted that:

> "Attempts to determine the rate of atmospheric reaeration without taking under consideration biologic activity have resulted in the publication of

vast amounts of erratic data which have been difficult to apply even to the body of water upon which the determinations were made."

Churchill (6) has presented data showing rates of oxygen recovery below impoundments for day and night conditions. Reaeration coefficients for the Watauga River were computed by M. Churchill, using the formula:

$$k_2 = \frac{\log D_A - \log D_B}{\text{Time of travel A to B}} \quad \ldots\ldots\ldots\ldots (23)$$

Comparison of daylight and darkness coefficients thur computed shows the following differences:

River Mile	Reaeration Coefficient Daylight	Darkness
33.85	6.02	3.53
32.43	4.80	2.40
31.45	4.60	2.04
30.43		

The conditions other than light for these data were identical, so that the marked differences between the daylight and darkness values of the reoxygenation coefficients can be attributed only to photosynthesis. Certainly these differences are significant.

The most recent work by engineers known to the writer which shows the significance of photosynthesis is that by R. V. Thomann et al (55). They used a three-cycle analysis to describe the variation of several water-quality characteristics of the Delaware River estuary. The three cycles are all assumed to be sinusoidal. In addition to the tidal cycle, they also considered the daily and seasonal variations. The sine curve attributed to the tidal effect has a period of slightly more than 12 hr. The daily, or diurnal, curve has a period of 24 hr. It is significant to note that the diurnal sine curve for oxygen presented as an example of the variation in the Delaware estuary (location unspecified) has a greater amplitude than the curve showing the effect of tide for the same station. Inasmuch as the 24-hr sine curve for oxygen concentration is generally the result of photosynthesis during daylight hours and its absence during darkness, it can be assumed that photosynthesis is a significant factor at that location in the estuary.

Several other references to photosynthesis appear in the technical literature familiar to sanitary engineers. Notable among these are the works of W. C. Purdy (41) on the Potomac River estuary, Purdy (42) on New York Harbor, W. Rudolfs and H. Heukelekian (41), C. K. Calvert (5), Purdy (42), G. J. Schroepfer (50), and G. M. Ridenour (43, 44). As recently as July, 1960 there appeared in this journal a most interesting paper by a group of biologists (B. W. Parker et al, 35) showing the diurnal variation of DO at a station above the tidal zone on the Delaware River. The frequent supersaturated DO values recorded are convincing evidence of photosynthetic oxygen production at that location (Riegelsville, N. J.).

Since World War II, scientists of various fields have begun working more closely with sanitary engineers in the problems of waste disposal and water-pollution control. Consequently, the subject of photosynthesis is being mentioned more and more in the engineering literature. Generally, however, the sanitary engineering publications have had little to say about primary production as a means of oxygenating natural waters.

In the literature of the other professional groups interested in water quality, one does not have to look far for information on photosynthesis. These groups have long since accepted the fact that algae and other aquatic plants contribute significant quantities of oxygen to the water. Their present concern with photosynthesis, or primary production, is directed toward means of its evaluation and measurement (J. H. Ryther et al., 48).

An extensive review of the literature of the sciences of limnology, biology, and oceangraphy on photosynthesis as it influences the oxygen balance in aquatic environments has been prepared by the writer and will be presented elsewhere (Hull, in press). This review, along with the writer's observations and measurements of primary production, has convinced the writer that photosynthesis is generally a very significant source of oxygen, and must be reckoned with in oxygen-balance studies. The almost universal occurrence of the process in water, as well as the ubiquity of algae, indicates strongly that photosynthesis is the rule rather that the exception. It therefore seems imperative, in the investigation of the oxygen balance of any water body, to consider this factor, whether the water be fresh, salt, or brackish. Without evidence other than "generally accepted opinion among sanitary engineers" to show definitely that photosynthesis is unimportant, the report of any oxygen-balance study omitting this factor must be considered incomplete, inconclusive, and probably erroneous. This applies to much of the existing literature of sanitary engineering on self-purification.

Perhaps Mr. O'Connor has negative evidence on photosynthesis in the Delaware and James estuaries. If so, it should be presented. Nevertheless, even if it can be shown with scientific observations that the neglect of photosynthesis is justified in these two estuaries, it should be emphasized that this factor cannot be assumed to be generally negligible in any estuary. The ease of determining, at least qualitatively, the occurrence or non-occurrence of photosynthesis obviates any need to rely on such an assumption without evidence.

There are several effects or products of photosynthesis which, if observed, serve to indicate the probable significance of this factor in the oxygen balance. An exhaustive search for available evidence of this kind for a given estuary is probably not justified, as it would require more time and expense than actual field measurements of primary production, and would be only qualitative. The writer has made a very hurried study of the information on the Delaware estuary available from the literature and from personal contacts with experts in possession of such information. It is emphasized that such a qualitative study is no substitute for quantitative productivity determinations.

Supporting the hypothesis that photosynthesis is significant in the polluted zone of the Delaware estuary are the following points:

(1) Plankton algae and benthic algae are present in reasonable abundance in the Delaware estuary (C. S. Boyer, 4; Public Health Service, 39; Ruth Patrick, 36). The plankton forms conceivably can be accounted for by transport into the pollution zone from fresh-water streams and from Delaware Bay. However, a healthy established population of the attached benthic forms means that photosynthesis is taking place in the polluted zone, at least in the shallow areas.

(2) Supersaturated DO values have been observed in the estuary above Philadelphia (A. J. Kaplovsky, 24), in tributaries contributing flow to the estuary (Kaplovsky, 24, Parker, et al, 35) and in the estuary below Bowers Beach, Delaware (D. P. de Sylva and F. A. Kalber, Jr., 7). Table 7 lists data

showing supersaturated DO values at various locations in the Delaware estuary between Reedy Island and the Burlington-Bristol Bridge. These are taken from unpublished data furnished by the Philadelphia Water Department and represent observations of several cooperating agencies which routinely study the Delaware. The occurrence of supersaturated DO concentrations of the magnitudes shown is generally taken as positive evidence of photosynthetic activity. On the other hand, the absence of supersaturation observations between Lehigh Avenue (mile 102.16) in Philadelphia and New Castle, Delaware (mile 67.68) cannot be taken as conclusive proof that photosynthesis does not occur. It appears reasonable to assume that photosynthesis probably occurs even in this polluted zone, unless algae are inhibited there by excessive turbidity or toxicity of wastes.

TABLE 7.—DELAWARE RIVER ESTUARY DATA SHOWING SUPERSATURATED D.O.[a]

River Mile (above Cape Henlopen Light)	Date, Year-Day[b]	Time 24-hr clock	Depth in feet	Chlorides, in ppm	Temp in °C	D. O. in ppm	D. O. in % saturation
60.96-4# (Pea Patch Island)	52-321	0936	20	4425	8.6	12.3	110
		0938	40	4555	8.6	12.5	112
			01	4295	8.7	12.2	109
54.86-4 (Reedy Island)	54-222	1624	20	4150	24.7	11.6	144
		1627	46	4105	24.7	11.1	137
		1621	01	3925	25.3	12.0	150
60.96-4 (Pea Patch Island)		1704	20	3165	25.3	10.8	134
			40	3425	25.0	10.5	130
			01	3280	25.3	11.1	138
67.68-4 (New Castle, Del.)		1744	01	2560	25.1	9.0	108
			20	2500	25.1	12.0	155
110.45-2 (Ben. Fr. Bridge)	54-067	0530	01	0017	7.0	13.4	110
54.86-4 (Reedy Island)	54-213	1338	51	4700	26.4	8.2	105
			01	4220	27.5	8.9	116
102.16-4 (Lehigh Avenue)	55-153	0854	03	11	22.8	10.0	112
117.81-3 (Burl.-Br. Bridge)	55-186	1131	03	10	28.9	8.7	112
110.45-2 (Ben. Fr. Bridge)	56-041	0730	01	--	2.0	15.2	110
117.81-2 (Burl.-Br. Bridge)	56-088	0750	01	--	5.4	14.6	116
	56-096	0715	01	--	9.0	13.0	112
117.81-4 (Burl.-Br. Bridge)	56-198	1006	03	5	23.9	10.6	123
	58-217	1335	03	5	27.5	8.9	111

[a] Unpublished data from files of Philadelphia Water Department.
[b] Days of year are numbered 1 through 366.
Numbers from 1-7 following the river mile designate sampling locations; location 1 is near west shore and 7 is near east shore of estuary.

(3) Mr. Kaplovsky (24) has observed that since the start of dredging to deepen the navigation channel in the Delaware River above Philadelphia, turbidity concentrations have been markedly higher than formerly recorded for the portion of the estuary between Trenton and the Philadelphia Navy Yard. At the same time, DO concentrations and pH values in the stretch have been significantly lower. These three changes, taken together, suggest the possibility that the increased turbidities have decreased light penetration and thereby lowered photosynthetic rates. It is conceivable, of course, that dredging has also increased the suspended BOD load by stirring up bottom deposits of organic matter. In this connection, however, Powell Engineers (37) found

little or no sludge deposits in the Delaware estuary channel above Philadelphia. Another possibility is that the increased suspended matter caused by dredging has created a favorable environment for bacteria, many types of which are known to multiply more rapidly when solid surfaces are present (C. E. ZoBell and D. Q. Anderson, 60; Messrs. Heukelekian and Heller, 16). Hence, the suspended solids would be expected to increase the bacterial growth rate (and therefore the BOD rate) even without increased concentrations of organic matter.

(4) Millions of pounds of seafood and other fish products are removed from the Delaware estuary annually. The Delaware is considered a biologically productive estuary (F. C. June and J. Reintjes, 23; C. N. Shuster, Jr., 51). Fish are high in protein content, and protein is about 50% carbon, according to C. R. Noller (30). This organic carbon was synthesized from inorganic carbon by the primary production of chlorophyl-bearing organisms, the "grasses of the sea." Some of the fish taken in the Delaware estuary are migratory and represent carbon that was originally fixed outside the estuary. Moreover, at least part of the basic food supply attracting migratory fish into the estuary was surely not synthesized in the estuary, but was imported in sea water and in terrestrial runoff, including man-made wastes. Nevertheless, if conditions are suitable to support millions of pounds of migratory and indigenous fin and shellfish, it is reasonable to assume primary production in the estuary. Primary production is accompanied by the release of oxygen, a molecule of oxygen for every atom of carbon fixed.

On the negative side, tending to discount photosynthesis as a major source of oxygen in the Delaware estuary, is the fact that the waters in the Delaware are relatively turbid compared to other estuaries where photosynthesis is known to be an important factor. Secchi-disc observations reported by de Sylva and Kalber (7) show low water transparency.

Taking all the evidence, together with the knowledge that algae and algae-released oxygen have generally been found wherever they have been sought, it is reasonable to assume that photosynthesis is a significant source of oxygen in the Delaware estuary. At any rate, it is far safer to assume that it is than to assume it is not. Whether it is a major source, a negligible source, or something in between, can be determined only by field measurements of production rates.

It should be noted that Mr. O'Connor is certainly not unaware of the effects of algae in the oxygenation of surface waters. In a paper by D. J. O'Connor and W. E. Dobbins (32), and in published discussions of that paper, the influence of algae was noted to explain lack of agreement between various values of the reaeration coefficient computed from observed DO and BOD data and values computed with a proposed "theoretical" formula for K_2. In view of this awareness, the author's present omission of photosynthetic oxygen production from the oxygen-balance theory for an estuary is all the more puzzling.

Still other sources of oxygen which have been considered in other estuaries may be important in the Delaware and James River estuaries. Messrs. Wheatland (58) and Gameson (11) have investigated the nitrogen and sulfur cycles as possible sources of oxygen in the Thames estuary. Mr. Gameson estimated that denitrification of nitrates entering the estuary at the head of tide contributed 56 tons of oxygen per day to the oxygen balance. An additional 22 tons per day was estimated for tributaries of the Thames. Gameson also considered the gain in oxygen in the Thames estuary resulting from reduction of sulfates followed by removal of the reduced sulfates by dredging and by

loss of hydrogen sulfide to the atmosphere. These losses were estimated to be equivalent to a gain in oxygen of about 16 tons per day. The total gain from denitrification and sulfate reduction was, therefore, about 94 tons of oxygen per day, a significant amount when compared to the average rate of oxygen utilization in the Thames estuary of about 700 tons per day.

Why emphasize photosynthesis and other possible sources of oxygen with such a lengthy discussion? Simply this: the only reason for proposing a theory to describe the oxygen balance is to allow one to predict the oxygen concentration for conditions other than those prevailing at any given time of observation. If the theory is correct and the correction factors are available to transpose the theory from observed conditions to the predicted conditions of temperature, dilution, waste loading, and other factors, it will be possible to forecast the oxygen concentration at a given time and place. However, if the theory is incomplete or erroneous, the predictions will be meaningless. For example, the temperature-correction coefficient for atmospheric reaeration (and even this is not known definitely) cannot be expected to apply to photosynthetic reoxygenation. Nor is there any reason to assume that the rate of change of the organic matter present as influenced by primary production will be adequately accounted for by a negative component of the coefficient of BOD removal, K_r. If photosynthesis is a significant source of oxygen and organic matter in an estuary, any theory which omits this factor cannot be used to predict DO concentrations.

If the only purpose of a mathematical theory is to fit a smooth curve through observed DO values, then Mr. O'Connor's formulas can probably be fitted reasonably well to the "sag" in most polluted estuaries, provided suitable coefficients are chosen. But if the formula does not include all factors causing a significant influence on the oxygen balance, such a smoothed curve cannot provide any more insight into the problem of waste treatment or of flow regulation than would a curve smoothed through the observed points by eye.

It has been almost forty years since W. C. Purdy (41), Kenneth Allen (1), and H. W. Streeter (22) pointed out the danger of omitting consideration of photosynthesis in a report by R. H. Gould (14) on New York Harbor. Since then, considerable evidence has been reported to indicate that photosynthesis and other factors are important. If sanitary engineers wish to continue omitting these factors from oxygen-balance studies, then it is time to begin gathering negative evidence to counteract the positive evidence accumulated over the last hundred years.

The expression for the atmospheric reaeration coefficient developed by Messrs. O'Connor and Dobbins (32) in an earlier paper and used by Mr. O'Connor in the present paper (Eq. 20) is another item to be viewed with caution. The equation for K_2, if valid, would be a most useful tool in oxygen-balance studies as it would provide a value for K_2 independent of DO, BOD, and time-of-travel measurements, which are difficult to determine accurately. However, the K_2 formula appears not to have been adequately tested. The principal support for the formula seems to be the close agreement between K_2 values calculated from the O'Connor-Dobbins equation and selected values from earlier literature calculated in the customary way using the oxygen-sag equation of Streeter and Phelps (53). It is significant to note that in selecting Streeter-Phelps values for comparison, many were discarded because of deviations presumed to be caused by algae or sludge deposits. The criteria used to judge whether algae influenced the Streeter-Phelps values of K_2 are

not clear in all cases. For one of the water bodies considered, San Diego Bay, algae effects were separated by light-and-dark-bottle tests, as reported by Messrs. Nusbaum and Miller (31). Concerning the Illinois River data, it was reported by W. H. Wisely and G. W. Klassen (60) that ". . . oxygen will be added to the river by . . . photosynthesis . . ." but that photosynthesis was not considered in their report. Messrs. O'Connor and Dobbins (32) stated that variation of DO concentrations at one station in the Illinois River were small, presumptive (but not conclusive) evidence that algae effects were negligible. For most of the streams used in the verification of the theory, however, no evidence was presented for or against algae influence. For one of these streams, the Ohio River, A. F. Bartsch (3) has since presented light-and-dark bottle evidence of considerable reoxygenation by photosynthesis. For another, the Illinois River, evidence of significant algae production has been given by C. A. Kofoid (26). In view of the evidence for the influence of photosynthesis in some of the waters, and the lack of evidence against algal effects in other waters considered by Messrs. O'Connor and Dobbins in the verification of the theoretical formula for K_2, this formula cannot yet be considered verified.

The K_2 formula (Eq. 20) should not be discarded, for such a device is urgently needed. However, before using it as a basis for a more complex theory of oxygen balance, the K_2 formula should be thoroughly tested under rigidly controlled conditions which positively eliminate photosynthesis, not to mention denitrification, sulfate reduction, and the potential differences between the coefficient of BOD removal and the deoxygenation coefficient. All of these factors are potential sources of error in the K_2 values computed from the oxygen-sag formula and used in the verification of the O'Connor-Dobbins relationship.

Because of the currently unsettled controversy over the solubility of oxygen in natural waters, as shown by the discrepancies among values reported by the American Public Health Association (2), G. A. Truesdale, A. L. Downing, and G. F. Lowden (56), and H. L. Elmore and T. W. Hayes (8), it would be helpful if all studies of oxygen balance would clearly specify which solubility tables were used. This would allow later evaluation and revision of the reports if and when the true solubility values are determined. It should be noted that an extensive research project is now underway at the Chesapeake Bay Institute of The Johns Hopkins University to resolve the reported differences in oxygen solubility.

The author has labeled some of the curves as Flood slack and Ebb slack. It would be preferable to conform consistently to the accepted, nonambiguous phraseology, high-water slack and low-water slack.

In order to distinguish the coefficient K_2, it is recommended that the definition of this symbol given in Appendix II be changed to read "coefficient of atmospheric reaeration." This would prevent confusion with the reoxygenating effects of photosynthesis and other factors.

In view of the findings of Messrs. Wheatland (58) and Gameson (11) on the reduction of sulfates in the Thames estuary, it would appear that a review is in order of Mr. O'Connor's use of sulfates as a "conservative" tracer for determination of the eddy-diffusion coefficient in the James River estuary.

Contrary to the tone of this discussion, the writer does not feel that the formulation of a theory adequate for predicting the oxygen concentrations in time and space for a natural water body is a hopeless task. However, such a theory will include more than deoxygenation by carbonaceous BOD and reoxygenation by exchange across the air-water interface. The factors which have

been considered in past studies are:

Oxygen Losses.—

(1) Total respiration, including carbonaceous BOD, nitrification, benthal oxygen demand;

(2) "Advective" losses, including oxygen in water diversions and water moving seaward;

(3) Chemical oxygen demand;

(4) Atmospheric deaeration (of supersaturated surface water);

(5) Dilution by oxygen-free water; and

(6) Ebullition of gases which purge oxygen from the water.

Oxygen Gains.—

(1) Atmospheric aeration;

(2) Photosynthetic oxygenation (plankton and benthos);

(3) Advective gains (fresh water inflow, waste discharges, sea water intrusion);

(4) Denitrification; and

(5) Sulfate reduction.

A single formula relating all of these factors, together with the necessary correction coefficients for temperature, sunlight intensity, turbidity, stream flow, and other controlling variables would be extremely complex and probably not amenable to computation except by high-speed automatic computers. Fortunately, computers are now available. When engineers begin to accept the importance of factors beyond the two traditional ones, first-stage BOD and atmospheric reaeration, progress will be made toward a theory describing the oxygen balance.

Acknowledgment.—Much of this discussion is based on material in the files of the Low-Flow Augmentation Project, Department of Sanitary Engineering and Water Resources, The Johns Hopkins University. The Low-Flow Project is currently supported by Research Grant RG-5312 (C3) from the National Institutes of Health, Public Health Service.

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DESIGN AND COST CONSIDERATIONS IN HIGH RATE SLUDGE DIGESTION[a]

Discussion by Samuel A. Greeley and C. Y. Hitchcock, Jr.

SAMUEL A. GREELEY,[1] F. ASCE.—This paper provides some interesting illustrations to illuminate the problem of high rate sludge digestion. In practice it was found that reliable operating information is scant and that very much more is needed on plant scale operation. It would be useful to have information like that presented by Mr. Estrada arranged and presented by the operators of treatment plants using high rate sludge digestion.

In his summary, Mr. Estrada appears to conclude that data is sufficient to demonstrate that gas circulation is effective for high rate digestion permitting reduced capacity of tanks. He also appears to conclude that mechanical agitation does not increase the rate of digestion and requires concentration to permit reducing tank capacity.

For the District of Columbia, a Board of Engineers, of which Frank A. Marston, Gustav J. Requardt, and the writer were members, studied the field of practice of high rate digestion as it was about two years ago and concluded that there was insufficient data to permit a selection of equipment for accomplishing homogeneity in the contents of a digestion tank. Until recently, much of the experience with gas recirculation was limited to agitating the upper parts of digestion tanks largely to reduce the formation of scum. One tank equipped with mechanical agitation and two tanks with gas agitation equipment have recently been placed in operation in four existing sludge digestion tanks at the Blue Plains plant of the District of Columbia. Information from this experience in parallel operation and elsewhere will be needed to supplement the records and data summarized by Mr. Estrada.

The Board of Engineers of the District of Columbia, while not reaching conclusions relative to the efficiency of several kinds of agitating facilities, did establish the following bases of design for loads on high rate sludge digestion operations:

Estimated Pounds of Raw Dry Suspended Solids per Cubic Foot of Tank Volume per Month	
Period	Pounds
Annual average	6.01
Five summer months	6.54
Maximum month	8.04

C. Y. HITCHCOCK, JR;[2] F. ASCE.—The writer believes that the conclusions drawn by Mr. Estrada from the data presented need some clarification. The

[a] May, 1960, by Alfred A. Estranda.
[1] Partner, Greeley and Hansen, Chicago, Ill.
[2] Proj. Engr., Metcalf Eddy Engineers, Boston, Mass.

terms "high-rate digestion" and "rate of digestion" are not synonymous. The former is a term used to denote digestion aided by mechanical mixing or gas recirculation. The "rate of digestion" is a fixed parameter which varies with the change in temperature from the mesophilic through the thermophilic ranges.

All "high-rate digestion" connotes to most of us is a high-solids loading per unit of tank volume. Two ways can be used to permit the higher loading, first by concentration in separate concentration tanks or by adequately controlling the sludge pumping, and second, by agitation of the entire tank's content. It seems perfectly obvious that, with careless operation, pumping 3% solids sludge to a digester would require twice the number of digesters for active digestion as would be the case if the raw sludge were pumped at six percent solids.

The agitation of the sludge by gas recirculation or by mechanical devices makes available a greater percentage of the total volume of the digestion tank for the digestion process. It is believed that this mixing adds anywhere from 50% to 100% to the effective volume of the digester over nonagitated tanks. In addition, mechanical or gas recirculation agitation provides uniformity of the digestion process throughout the tank volume and is an added feature available toward good operation.

The writer acknowledges that the makeup of sludge varies considerably from place to place and that each sludge should be considered individually but he hopes that the State Health Departments will allow higher solids loadings in sludge digestion tanks where agitation of the tank contents will be accomplished by either gas recirculation or mechanical mixing.

The writer also would like to have the phrase "high-rate digestion" changed to "high solids digestion," thus giving a truer meaning to the terminology used. In this way, it would not be confused with "rate of digestion" which varies with temperature.

As sludge facilities are a large cost factor in the construction and operation of a sewage treatment plant, everything should be done to minimize the sludge tank capacity required by allowing designers to take advantage of all the information presently available for "high loading digesters."

PROCEEDINGS PAPERS

The technical papers published in the past year are identified by number below. Technical-division sponsorship is indicated by an abbreviation at the end of each Paper Number, the symbols referring to: Air Transport (AT), City Planning (CP), Construction (CO), Engineering Mechanics (EM), Highway (HW), Hydraulics (HY), Irrigation and Drainage (IR), Pipeline (PL), Power (PO), Sanitary Engineering (SA), Soil Mechanics and Foundations (SM), Structural (ST), Surveying and Mapping (SU), and Waterways and Harbors (WW), divisions. Papers sponsored by the Department of Conditions of Practice are identified by the symbols (PP). For titles and order coupons, refer to the appropriate issue of "Civil Engineering." Beginning with Volume 82 (January 1956) papers were published in Journals of the various Technical Divisions. To locate papers in the Journals, the symbols after the paper number are followed by a numeral designating the issue of a particular Journal in which the paper appeared. For example, Paper 2270 is identified as 2270(ST9) which indicates that the paper is contained in the ninth issue of the Journal of the Structural Division during 1959.

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c. Discussion of several papers, grouped by divisions.

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NOVEMBER 1960 — 40 NO. SA 6
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Proceedings of the American Society of Civil Engineers

NEWS

November, 1960

EDITORIAL

NEW VISTAS IN SANITARY ENGINEERING

In the last issue of the Newsletter, we presented the text of the Notice of the Secretary of Health, Education, and Welfare and Findings, Conclusions, and Recommendations of the Hearing Board as related to interstate pollution of the Missouri River in the Kansas City Metropolitan area. Also, in past Newsletters, reports have been made on other widely separated enforcement cases.

In order that sanitary engineers may gain a wider knowledge of this activity as a whole, we have reproduced the current Status of Interstate Enforcement Cases which gives a brief picture of Federal activity in this field.

STATUS OF INTERSTATE ENFORCEMENT CASES

1. Corney Creek (Arkansas-Louisiana)—Formal Hearing January 16 and 17, 1957. All oil wells within the purview of the Hearing are now controlling their wastes and the stream is recovering. New oil wells have been opened within the area and the matter of control of these wastes is being handled by the Arkansas Water Pollution Control Agency.

2. Big Blue River (Nebraska-Kansas)—Conference May 3, 1957. Nine communities and the one industry within the conference area have completed construction of remedial facilities; six have such facilities under construction, five have been offered construction grants and three have taken no action.

3. Missouri River-Omaha, Nebraska Area (Nebraska-Kansas-North Dakota-Iowa)—Conference held June 14, 1957. Successful bond elections were held by Omaha, Nebraska, November 4, 1958 and May 10, 1960. Two more

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elections are being planned, one for November 1960 and one for May 1961. If both of the latter are successful, the city will have raised sufficient funds to finance the remedial works contemplated by the conferees. Some of the agreed upon facilities have been constructed, some are under construction, and final plans and specifications have been completed for all. Other municipalities in the conference area have completed construction of the required remedial facilities, or have such in the planning stage.

4. Missouri River-St. Joseph, Missouri Area (Missouri-Kansas)—Conference held June 11, 1957. Atchison, Kansas has remedial works under construction. Leavenworth, Kansas plans to let a construction contract by September 30, 1960. St. Joseph, Missouri and its associated industries failed to take the action recommended by the conferees and therefore the Secretary of Health, Education and Welfare called a public hearing. It was held July 27-30, 1959. Thereafter, the Secretary, on August 12, 1959, issued to the city of St. Joseph and its 18 associated industries, a notice to cease and desist polluting the river and requiring the city and the industries to provide remedial facilities according to a time schedule recommended by the Hearing Board, and to have completed such by June 1, 1963. The time schedule required the city to hold a bond election for financing the required remedial works on, or before, June 1, 1960 and to proceed with final plans and specifications by July 1, 1960. The election was held May 21, 1960, but the bond issue was defeated. The city failed to proceed with final plans and specifications by July 1, 1960. On August 1, 1960, the Secretary of Health, Education and Welfare referred the matter to the Attorney General for court action as provided for in section 8(f) of P.L. 660. 17 of the 18 industries plan to install their own remedial facilities.

5. Potomac River-Washington Metropolitan Area (District of Columbia-Maryland-Virginia)—First session of Conference held August 22, 1957; second session on February 13, 1958. D.C. Blue Plains Plant completed, improvements continuing; planning and construction in line with Plan C continues. Commensurate action being taken by Maryland and by Virginia communities.

6. Missouri River-Kansas Cities Metropolitan Area (Kansas-Missouri)—Conference held December 3, 1957. Kansas City, Kansas, is building interceptor sewers and purchasing sites for future sewage treatment plants; has scheduled bond election for November 1960. North Kansas City, Missouri, Engineering Report approved by State water pollution control agency. Kansas City, Missouri, has complete preliminary Engineering Report. However, the action taken is not in substantial compliance with time schedule established by the conferees. Wherefore, a public hearing was held in Kansas City, Missouri, June 13-17, 1960, and the Secretary, on June 30, 1960, issued a cease and desist Notice to Kansas City, Kansas; Kansas City, Missouri; North Kansas City, Missouri and the Kaw Valley and Fairfax drainage districts of Kansas and eleven industrial establishments.

7. Mississippi River-St. Louis Metropolitan Area (Missouri-Illinois)—Conference March 4, 1958. St. Louis Metropolitan Sewer District and Illinois communities are preparing plans and specifications for remedial facilities. St. Louis Metropolitan Sewer District is working with industries to reduce amount of industrial wastes to "practical minimum"; Illinois

industries are either providing satisfactory control or arranging to be served by municipal systems.

8. Animas River (Colorado-New Mexico)—First session of conference held April 29, 1958; second session held June 24, 1959. Remedial action taken by the Vanadium Corporation of America. Evaluation was made in November 1959. Surveillance is continuing.

9. Missouri River-Sioux City Area (South Dakota-Iowa-Nebraska-Missouri-Kansas)—Conference held June 24, 1958. In compliance with conference recommendations, Blair, Nebraska and Elk Point, South Dakota have completed construction of remedial facilities; Yankton and Vermillion, South Dakota have remedial works in planning stage. Sioux City, Iowa, did not take action in compliance with agreements of the conferees; consequently, a public hearing was held in Sioux City March 23-27, 1959. The Secretary of Health, Education, and Welfare thereafter, issued a Notice dated April 7, 1959, directing Sioux City and associated industries to cease and desist their pollution of the river and to complete remedial action by March 1, 1963. Action is being taken but the time schedule is not being fully adherred to by Sioux City. All industries have requested service of the city.

10. Columbia River (Washington-Oregon)—Conference-1st Session-September 10 and 11, 1958; 2nd Session held September 3 and 4, 1959. Conferees established time schedule for remedial action by communities and industries.

11. Bear River (Idaho-Wyoming-Utah)—First session of conference held October 8, 1958; second session was held July 19, 1960, at Logan, Utah. While the conferees determined that interstate pollution existed in the Bear and the Cub Rivers and Worm Creek, no time schedule for remedial action was established. The States of Idaho and Utah will advise the Surgeon General by August 19, 1960, whether or not a schedule will be established. The conferees found intrastate pollution existing in the Evanston, Wyoming area. Nevertheless, Wyoming will take action to control that pollution.

12. Colorado River and all tributaries (Colorado-Utah-Arizona-Nevada-California-New Mexico-Wyoming)—First session of conference held January 13, 1960; second session to be held not later than April 30, 1961, to evaluate progress of cooperative Federal-State investigation and study and receive recommendations for further action. The investigation is under way.

13. North Fork of the Holston River (Tennessee-Virginia)—On May 31, 1960, the Tennessee Stream Pollution Control Board requested the Surgeon General to call a conference under section 8 of the Federal Water Pollution Control Act. The conference is scheduled for September 28, 1960, at Kingsport, Tennessee.

DID YOU KNOW THAT

DR. MYRON COOK RAND joined the faculty of the Civil Engineering Department of Syracuse University in September. Dr. Rand will serve in the capacity of Associate Professor in the graduate and research programs in Sanitary Engineering.

THOMAS A. McCANN, Mayor of Fort Worth, Texas has been named by President Eisenhower to a three-year term on the Federal Water Pollution Control Advisory Board. Mayor McCann is president of a construction firm and has ranching interests in three Texas counties. He also serves as a director of the Western Savings and Loan Association, the Texas Consumers Finance Corporation, the Hurst State Bank, and the National Investment Life Insurance Company.

DR. CLAIR S. BORUFF of Peoria, Illinois has also been named by President Eisenhower for a three-year term on the Federal Water Pollution Control Advisory Board. Dr. Boruff, technical director for Hiram Walker and Sons, received his philosophy degree in sanitary chemistry from the University of Illinois in 1931. He once served as an associate professor of Monmouth College and as chief research chemist for the Illinois State Water Survey and, in 1957, was appointed industrial representative to the Illinois State Sanitary Water Board.

The appointments of Mayor McCann and Dr. Boruff fill two of the three existing vacancies on the Board caused by the expiration of the terms of the following Board members: I.T. Bode, former director of the Missouri Conservation Commission; Anton Hulman, Jr., chairman of the Indiana Flood Control and Water Resources Commission; and William F. Duckworth, mayor of the City of Norfolk, Virginia.

SECRETARY FLEMING SETS GOALS FOR NATIONAL WATER POLLUTION CONFERENCE

Arthur S. Flemming, Secretary of Health, Education, and Welfare, has asked for "vigorous discussion" of water management problems when the National Conference on Water Pollution meets in Washington next December 12, 13, and 14.

At a meeting of the Conference's 35-man steering committee held on August 11, Secretary Flemming told an audience of professional, industrial, and civic leaders that the Conference will have a unique opportunity at its meeting to develop views which can be placed before an incoming Congress and a new administration.

He set two goals for the Conference—that it try to obtain substantial agreement (1) on national goals for water pollution control, and (2) on the specific programs needed to reach these goals. He noted that, at a citizen's conference, unanimity of opinion on highly controversial issues cannot be expected. "But this is a healthy democratic process," he said, "and is the way in which we make progress in this country in this issue as well as in many other issues."

Surgeon General Leroy E. Burney pointed out to the committee that the United States is headed for a water crisis in the current decade unless the American people do a much better job of cleaning up the country's water resources.

"Since the start of World War II," Dr. Burney said, "construction of water supply and pollution control facilities has lagged far behind national needs. These needs will continue to grow during the 1960's as the result of population increases, the further concentration of people in metropolitan centers, and sharp increases in the use of water by households, farms, and industry.

"Partly because of public apathy toward the water problem," Dr. Burney told the committee, "the United States has accumulated a huge national deficit in needed facilities.

"In a number of communities and in some river basins, citizens, governmental authorities, and industry have done a good job of cleaning up rivers and other water sources. But in many other places much more aggressive action is necessary if mounting demands for clean water are to be met and if the public health is to be protected.

It is time we faced the fact that the problem of water resources is urgent and that we can no longer neglect this vital segment of the national economy without storing up serious trouble for the future. We need to apply more sanity to sanitation."

The Conference steering committee under the chairmanship of Frank A. Butrico, Executive Secretary of the Conference, approved a meeting format calling for plenary sessions on its first and third days and four concurrent panel sessions on the second day. Subjects of the four panel meetings were tentatively set as "Water Pollution and Our Changing Times," "Meeting the Growing Competition for water," "Keeping Water Clean," and "Research and Training."

CALIFORNIA TO HOST 88TH ANNUAL MEETING, APHA, IN SAN FRANCISCO October 31 - November 4

With an anticipated attendance of more than 5,000 public health workers from the 50 states and other parts of the world, the 88th annual meeting of the American Public Health Association will be held in San Francisco from October 31 through November 4. This is the first annual meeting to be held on the West Coast since 1951.

Presiding over the general sessions will be this year's president, Dr. Malcolm H. Merrill, California State Director of Public Health.

In tune with the times, the convention has chosen as its theme "Man and His Changing Environment." The meeting will bring together outstanding public health leaders for presentation of papers and discussion of emerging problems related to the changes taking place so rapidly in man's way of living. Air pollution, radiological health, geriatrics and medical care for the aged, newer concepts applicable to epidemiology, innovations in laboratory procedures, and pressing problems in the wide field of chronic diseases are examples of the topics with which participants will concern themselves during a busy five days. Some 400 speakers will focus attention on current public health progress in more than 100 scientific sessions.

Attendance at the APHA meeting is open to members and nonmembers alike. A registration fee of $8 entitles the delegate to all privileges of the meeting.

One day registrations of $2 are also available to personnel of health departments when arrangements are made in advance by the health officer with the Association at 1790 Broadway, New York 19, New York.

Thirty-seven related organizations and 12 public health alumni groups have scheduled their annual meetings immediately preceding or during the APHA meeting. They will also meet jointly with APHA sections during the week.

The San Francisco Civic Auditorium will serve as headquarters for the meeting, and most of the scientific sessions will be held there. However, during the week numerous meetings will be going on in the various convention hotels as well as in the auditorium. These include the Jack Tar, Sheraton-Palace and Whitcomb Hotels.

UNIVERSITY OF ILLINOIS
THIRD SANITARY ENGINEERING CONFERENCE ANNOUNCED

Disinfection and Chemical Oxidation in Water and Waste Treatment is the title of the Third Sanitary Engineering Conference to be held in Urbana, Illinois, on January 31, and February 1, 1961. The conference is sponsored jointly by the Division of Sanitary Engineering, Illinois Department of Public Health and the Department of Civil Engineering, University of Illinois. Earlier conferences have been on the subjects of Waterworks Safety and Radiological Aspects of Public Water Supplies. Further information may be obtained from Ben B. Ewing, Associate Professor of Sanitary Engineering, University of Illinois, Urbana or from C. W. Klassen, Chief Sanitary Engineer, Department of Public Health, Springfield, Illinois.

HILO TSUNAMI DISASTER

Dawn, May 23, Hilo, Hawaii: Unknown number of people injured, killed or homeless.

All electrical and gas power—out.

Telephone communication—non-existent.

The only plant for the pasteurization of milk—demolished.

Sewage pumping plants—inoperable.

These were only a few of the problems facing public health workers and the people of Hilo in the wake of the first major TSUNAMI (seismic wave) disaster since 1946.

At 8:30 p.m. the previous night, the State of Hawaii had been put on Tidal Wave Alert status. All persons in low-lying coastal areas were instructed to evacuate to higher ground. The cause of the expected wave had been the earthquakes in Chile some 6,000 miles away. The size of the wave, which was expected to reach Hawaii at midnight, could not be predicted.

Although many beach areas of the State were affected, the greatest damage was to the City of Hilo on the Island of Hawaii. Hilo had been the scene of tidal wave tragedy in 1946 when it was hit by a wave originating in the Aleutian Islands. The Chilean wave severely damaged over 180 acres of industrial, business, and residential areas. The major portion of the Hilo waterfront was wiped clean.

Water:

Fortunately there were no breaks in the main water distribution system. The destruction of buildings snapped house and industrial service lines resulting in a reduction of water pressure. As a safety precaution, health officials recommended an increase in the chlorine dosage. As an extra precaution, Dr. Bockrath recommended the boiling of drinking water. Some ingenious methods were used until power was restored. Charcoal fires and oil stoves were much in use.

Sewage Disposal:

Of the three sewage pumping plants, two were destroyed and the third rendered inoperable because of water damage to the pumps, and lack of power. The bulk of the sewage flows by gravity through an 1800' foot outfall into Hilo Bay. Later inspection showed that this line had not been damaged by the wave.

As this line was not damaged and supplementary lines could be used the removal of liquid wastes was possible. As come untreated sewage was being discharged into the bay along the shoreline, signs were posted along the shore warning the people not to use the bay shore waters.

That the public health job was well done is indicated by the complete lack of any disaster-born disease.

* * *

Water Supply & Pollution Control

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WATER QUALITY SYMPOSIUM HELD

A Water Quality Measurement and Instrumentation Symposium was held August 29-31 in Cincinnati, O., at the Hotel Sinton and at the Public Health Service's Robert A. Taft Sanitary Engineering Center.

The three-day symposium, the first on this subject sponsored by the Public Health Service, consisted of 28 technical presentations on four major topics: (1) the definition of the role of water quality measurement in water resources management; (2) review in broad terms of the methodology, collection and utilization of water quality data; (3) the review of available instrumentation and the highlighting of developmental needs; and (4) the discussion of methods of data transmission, distribution, evaluation, storage and other factors concerned with data handling and utilization.

Particular emphasis was placed on the availability of and/or the need for further development of automatic instrumentation for the measurement of water quality. Technical presentations were made by representatives of PHS, state and local agencies, universities and related industries.

FEDERAL WPC ADVISORY BOARD INSPECTS FEDERAL INSTALLATIONS AT SAN FRANCISCO BAY

The Federal Water Pollution Control Advisory Board took a firsthand look at pollution by Federal installations in San Francisco Bay during the Board's 2-day meeting in San Francisco September 7-8.

This was the third session this year for the nine-member Board which is appointed by the President to advise the Surgeon General of the Public Health Service on problems in water pollution.

The California State Water Pollution Control Board joined with the Federal Board on September 7 for a boat-plane tour of pollution in the Bay area.

Abatement of pollution originating in Federal installations has been difficult for most States, but the problem has been more acute in the coastal States, where more Federal establishments are located.

Two newly appointed members of the Federal Board, named recently by President Eisenhower to three-year terms, joined other Board members for the San Francisco session. They are Thomas A. McCann, mayor of Fort Worth, Texas, and Dr. Clair S. Boruff of Peoria, Illinois, technical director of Hiram Walker and Sons, distillers.

Other Board members are: Seth Gordon of Sacramento, California, former director of Pennsylvania and California wildlife agencies; Frank E. Long of Buffalo, Wyoming, member of the Wyoming Stream Pollution Control Advisory

Council; William S. Wise of Hartford, Connecticut, director of the Connecticut Water Resources Commission and member of the New England Interstate Water Pollution Control Commision; John S. Samson, Omaha, Nebraska attorney and former chairman of the Nebraska Water Pollution Control Council, Dr. Russell E. Teague of Frankfort, Kentucky, director of the Kentucky State Health Department, secretary of the Kentucky Water Pollution Control Commission, and former chairman of the Ohio River Valley Water Sanitation Commission, and John Charles Daly of New York City, a vice president of the American Broadcasting Company.

CONFERENCES ON INTERSTATE POLLUTION OF BEAR RIVER

The second session of a conference on pollution of the Bear River (Utah-Wyoming-Idaho) was held on July 19, 1960 at Logan, Utah under provisions of the Federal Water Pollution Control Act.

Several municipalities and industries in Idaho were cited as contributing pollution from Idaho to Utah. It was agreed that both Idaho and Utah would submit to the Surgeon General of PHS schedules for proposed remedial action applicable to the municipalities and industries named at the conference.

ENFORCING WATER POLLUTION CONTROL

Secretary of Health, Education, and Welfare Arthur S. Flemming has asked the Department of Justice to bring suit on behalf of the United States to secure abatement of pollution of the Missouri River by the City of St. Joseph, Missouri.

Such a suit would be the first to be instituted under the enforcement provisions of the Federal Water Pollution Control Act.

The Kansas State Board of Health has requested that the matter be referred to the Department of Justice and the Missouri Water Pollution Control Board has consented to the action. The Federal Water Pollution Control Act requires only the consent of the State in which the pollution originates or the request of the downstream State.

A notice issued by Secretary Flemming on August 12, 1959, directed that the city and 18 industrial establishments build and put into operation by June 1, 1963, "proper, adequate, and effective municipal and industrial sewage and waste collection, treatment, and disposal facilities."

This was recommended by a hearing board appointed by the Secretary after the city and the industries failed to comply voluntarily with recommendations of the Surgeon General of the Public Health Service. The hearing board found that pollution of the Missouri River by the City of St. Joseph endangers the health and welfare of persons in the State of Kansas.

A timetable recommended by the hearing board called for a bond election by June 1, 1960, to finance the necessary municipal facilities and a notice to the city engineer by July 1, 1960, to proceed with the preparation of final plans and specifications.

In his notice of August 12, 1959, the Secretary said he found that compliance with the timetable recommended by the hearing board was "necessary to constitute action reasonably calculated to secure abatement" of pollution at St. Joseph by June 1, 1963.

The election was held on May 21 and the bond issue was defeated. The preparation of plans and specifications has not been ordered.

Industries outside of St. Joseph are proceeding with preparations for

construction of their own abatement works in accordance with the timetable recommended by the hearing board.

JOHNS HOPKINS ANNOUNCES SEMINAR REPORT

The Department of Sanitary Engineering and Water Resources' Advanced Seminar has prepared a report on "A Method for Evaluating the Water Supply and Demand in a Region." Coming as it does, on the heels of the recent Senate Select Committee hearings on water resources policy, this report may be of interest to those ASCE members working on water resources evaluation. Copies will be sent to those interested persons writing in care of John T. O'Conner, Johns Hopkins University, School of Engineering, Department of Sanitary Engineering and Water Resources, Baltimore 18, Maryland.

WASHINGTON, D. C. VOTES TO CLEAN UP POTOMAC

On September 14, 1960, Surgeon General Leroy E. Burney said that passage of legislation to increase the borrowing capacity of the District of Columbia marks a major step forward in the long history of efforts to reduce pollution in the Potomac River.

Elimination of up to 75 percent of the untreated sewage reaching the Potomac and Anacostia Rivers as a result of storm water overflows would be accomplished by the separation of storm and sanitary sewers in selected areas of the District, and a system of river-side interceptor sewers.

Public Law 86-711, signed by the President on September 6, increases the maximum amount which may be borrowed (from $5 million to $32 million) by the District of Columbia for use in the construction and improvement of its sanitary and combined sewer systems. It is in accord with a recommendation made by conferees representing the water pollution control agencies of the District of Columbia, Maryland, Virginia, the Interstate Commission on the Potomac River Basin, and the Public Health Service, in February, 1958. The conferees recommended that remedial facilities be completed by the end of 1966; and that appropriate financial arrangements be made to accomplish this.

ST. LOUIS PROPOSES NEW TRUNK SEWER

A $4.75 million trunk sewer for the Gravois Creek area of south St. Louis county and a $10,896,000 revenue bond issue for a trunk sewer and treatment plant for the Coldwater Creek area of north St. Louis county will be submitted to voters in the two watersheds on August 30, 1960, it has been announced by the Metropolitan Sewer District.

The Gravois Creek trunk sewer would bottle up in a pipe all the sewage now flowing through the creek and discharge into the Mississippi River near a point where MSD expects to eventually construct one of several large treatment plants, as part of its District-wide pollution abatement program. It would serve an ultimate population of about 245,000 persons in a 25-square mile watershed.

The Coldwater Creek proposal would finance the trunk sewer and treatment plant by means of revenue bonds issued over a 30-year period; the area now has a population of about 110,000 and would serve an ultimate potential population of about 230,000. The watershed is about 60 square miles in size.

The proposed facilities include a 12.3 mile trunk sewer with a capacity to serve 230,000 persons which would drain into a large treatment plant to be

located near the point where Old Halls Ferry Rd. crosses the creek. The plant would be large enough to completely treat the sewage of about 200,000 persons and could be expanded to handle the load from an additional 30,000 persons after 1980, when the ultimate population is expected to be reached.

Peter F. Mattei, executive director of the Metropolitan Sewer District explained: "The urgency of both bond issues simply cannot be stressed too strongly. The two creeks are running full to their banks with raw and only partially treated sewage that is literally teeming with raw human feces, garbage, trash and sludge from septic tanks and improperly treated sewage in an advanced stage of decomposition. Bubbles caused by gas released from rotting solids under the water dimple the surface of the creeks and are often followed by blobs of revolting, horrible-smelling decomposing sludge which float up from the creek bed.

"These conditions cause odors that are so foul and obnoxious that they drive nearby homeowners indoors on hot nights and week ends, and are so potent that—once drawn into the house by fans—they cannot be driven back out.

"The creeks are enormous incubators for such terrible diseases (or their carriers) as typhoid, polio, dysentery, and St. Louis encephalitis, which devastated the St. Louis area in 1933, killing or paralyzing more than 1000 persons. It flared up again in 1937 and, today, is the most prominent producer of epidemic encephalitis in the United States.

"Homeowners should realize," Mattel continued, "that encephalitis and other sewage bred diseases are carried as far as 12 miles from the creeks in which they breed by mosquitoes, flies and other 'unguided missles.' The present condition of the creeks thus poses a very real and terrible threat to the health and safety of familes throughout each watershed."

WEST VIRGINIA ESTABLISHES STATE WATER QUALITY NETWORK

A network of water quality monitoring stations has been established by the State Water Resources Commission. The purpose of the network is to provide a continuous record of water quality at selected points throughout the State. The information, to be published yearly, will provide a basis for planned industrial and recreational development and water pollution control.

Routine sampling of all major streams was done after World War II but was discontinued about 1955 due to lack of personnel. The work at that time consisted mostly of intensive sampling during the summer months in connection with limited or local programs. The data collected were never published.

Under the newly established monitoring program the number of stations has been reduced but the streams will be sampled on a year-around basis. At first, each station will be sampled once per month, with more frequent sampling later on if possible.

Thirty-three stations have been set up including 11 points in the Kanawha Basin, 9 in the Monongahela, 5 in the Little Kanawha, 4 in the Potomac, and 2 each in the Tug Fork and Guyandot. The state program will not extend into the Ohio River Basin, since similar work along that stream is being carried out by the Ohio River Valley Water Sanitation Commission of which West Virginia is a member.

MONITORING OF KANAWHA RIVER, W. VA., STARTED BY INDUSTRIES

Daily sampling at five points along the Kanawha River was started on July 1 by the industrial plants operating along the river.

The program is a cooperative one between industry and the Water Resources Commission and is coordinated through the Kanawha River Industrial Advisory Committee. Daily analyses are being made by the cooperating industries throughout the summer for dissolved oxygen, pH, chemical oxygen demand, ammonia and threshold odor. Weekly samples are being analyzed by the Water Resources Commission for biochemical oxygen demand. Sampling will be done twice a week during winter.

Samples are taken at the Chelyan Bridge and the Kanawha City Bridge by the DuPont Company. The Dunbar Bridge is sampled by Westvaco and analyzed by Union Carbide. River samples are collected and analyzed at the St. Albans Bridge by Union Carbide and Goodrich-Gulf while the Winfield Bridge samples are the responsibility of the industries in the Nitro area.

The main purpose of the sampling program is to give the Commission and the cooperating industries a better understanding of the day-to-day variations in waste loads over a long period of time.

It is believed that the daily tests will enable the Commission to anticipate conditions leading up to fish kills before they occur, although it is doubtful if such knowledge can be used to minimize the extent of the expected kills.

The Commission has reason to believe that as the industries build treatment plants and the river improves, fish populations will be increased during the higher flow periods only to be killed off in greater numbers when the oxygen is depleted during low flow periods. This is expected to continue even after the 1963 deadline for the 40 per cent reduction in industrial waste loads until the Kanawha River is restored to a condition suitable as a rough fish habitat the year around.

WATERWORKS WARNING NETWORK PLAN FOR LOWER MISSISSIPPI IS ANNOUNCED

Complete details of a formal water works warning network plan for the Lower Mississippi River were announced in June by John Trygg, director of the division of public health engineering.

Participating in the system would be the water works operators and officials, the state board of health, the Louisiana Stream Control Commission, and state industries.

"The system would provide a reasonable safeguard to the quality of water going to the consumers," Mr. Trygg said.

The published plan sets up specific procedures to be followed and lists the responsible persons to be contacted in case of reported accidental discharges by industry into the Mississippi River. Mr. Trygg noted that the warning system will also fit in well with Civil Defense functions.

METHODS FOR COLLECTION AND ANALYSIS OF WATER SAMPLES RE-RELEASED

Publication of a Geological Survey manual describing methods for collecting, preserving, and analyzing water samples was announced today by the Department of the Interior.

Since the procedures are applicable to the study of most natural waters, the manual is expected to become a general reference work for water chemists and a field and laboratory guide for those engaged in water-resources investigations, Survey officials said.

The manual represents many years of experience in water chemistry by the

Geological Survey, and the methods described are standard in the Survey. However, the manual should be valuable to all those who make detained analyses of water. Among the topics discussed are selection of sampling sites, frequency of sampling, field equipment, instruments, preservaties and fixatives, and analytical techniques. Seventy-seven laboratory and field procedures are given for determining fifty-three properties of water. Many new instruments and analytical techniques are described and discussed.

The manual, published as Geological Survey Water Supply Paper 1454, entitled, "Methods for collection and analysis of water samples," was written by F.H. Rainwater and L.L. Thatcher. It consists of 301 pages including 17 figures and 3 tables. Copies of the manual may be purchased for $1.50 from the Superintendent of Documents, Government Printing Office, Washington 25, D.C.

FISH KILL SURVEY UNDER WAY

How many tons of fish are destroyed each year by pollution of the Nation's waters? Until now, no one really knew the answer.

To provide this answer, the Public Health Service on June 1, 1960, inaugurated a nationwide reporting system.

Surgeon General Leroy E. Burney initiated the project with a letter to State fish and game agencies, enlisting their help. He wrote: "Increasing numbers of fish kills in both fresh and coastal waters raise a warning that there are at times lethal quantities of toxic substances in our waters. They result in great economic and recreational losses to commercial and sport fishermen."

Virtually all of the State fish and game agencies had responded enthusiastically to Dr. Burney's solicitation by August 1, and indicated their willingness to participate fully in the project.

More than 50 pollution-caused fish kills were reported in the first 2 months of the survey, according to the Basic Data Branch of the Division of Water Supply and Pollution Control. This Branch is serving as the focal point for reporting all fish kills from the States, and will make its first national report in October, based on reports from the States. Thereafter, fish kill data will be published quarterly and annually.

The Public Health Service maintains a National Water Quality Network of 75 water sampling stations across the Nation, and this project is another step toward effectively determining on a longrange basis what is happening to our Nation's water resources, as well as forecasting the effects of such pollution on the physical and economic health of the United States.

THREE NEW OFFICE OF SALINE WATER RESEARCH AND DEVELOPMENT PROGRESS REPORTS NOW AVAILABLE TO PUBLIC

Three new technical reports of the Office of Saline Water have been published and are for sale by the Department of Commerce, the Department of the Interior announced today.

The reports are: "Development of the Solvent Demineralization of Saline Water," "Research on and Development of Ion-Selective and Ion-Specific Membranes for use in the Large-Scale, Low-Cost Demineralization of Saline Waters by Selective Electrodialysis," and "Development of the Zone-Purification Process for Preparing Potable Water from Sea Water."

"Development of the Solvent Demineralization of Saline Water," is a report of experimental work conducted by the Texas A & M Research Foundation under contract with the Department of the Interior's Office of Saline Water.

The report provides solubility and equilibrium data for a variety of solvents that have been investigated and evaluated in detail for the desalination process. Operational data for the laboratory model of the extraction process are reported and a cost equation is developed to allow rapid evaluation of the results produced by different solvents and by various operating conditions.

"Research on and Development of Ion-Selective and Ion-Specific Membranes for use in the Large-Scale, Low Cost Demineralization of Saline Waters by Selective Electrodialysis," has been prepared for the Office of Saline Water by the Polytechnic Institute of Brooklyn. The purpose of this investigation was to study known membrane systems which might be more permeable to sulfate than to chloride, and to attempt the preparation of membranes of improved specificity. The report contains the results of experimental work carried out under this contract as well as a discussion of the theoretical potential and general considerations in membrane phenomena.

"Development of the Zone-Purification Process for Preparing Potable Water from Sea Water," has been prepared by the Battelle Memorial Institute for the Office of Saline Water. The objective of this contract was to obtain the optimum economic potential of the zone-freezing process. The study has provided a cost estimate of $9.59 per 1,000 gallons for 100,000 gallons per day plant and $4.21 per 1,000 gallons for a 10-million gallons per day plant. As a result of this study it is apparent that the zone-freezing system studied is not competitive with other freezing systems now under development and it is unlikely that further investigation of this system would disclose any practical means of reducing the costs for the zone-freezing process to any significant degree.

Copies of these reports are for sale by the United States Department of Commerce, Office of Technical Services, Washington 25, D.C.

The price of "Development of the Solvent Demineralization of Saline Water," is $2.25. To order this report specify order number PB 161769.

"Research on and Development of Ion-Selective and Ion-Specific Membranes for use in the Large-Scale, Low-Cost Demineralization of Saline Waters by Selective Electrodialysis," sells for $2.00. To order this report specify number PB 161694.

To obtain "Development of the Zone-Purification Process for Preparing Potable Water from Sea Water," specify order number PB 161766. The price is $1.00.

BIDS ASKED FOR SALINE WATER CONVERSION PLANT

Construction specifications for the one-million gallons per day saline water conversion demonstration plant to be erected on Point Loma at San Diego, California, were made available to bidders on September 1.

Dr. A. L. Miller, Director of the Office of Saline Water, stated that the specifications called for work to be performed under a single contractor responsible for complete construction and start-up operation of the conversion plant which will utilize a multi-stage flash distillation process. The plant will use a conventional steam boiler with heat supplied by fuel oil. The City of San Diego will purchase the product water from the plant. The California Department of Water Resources is assisting in the project by providing up to 50 percent of the design and construction costs, or $1.25 million which ever is least. Describing the operation Dr. Miller said, "In flash distillation sea water is progressively heated and then introduced into a large chamber where a pressure just below the boiling point of the hot brine is maintained. When the brine

enters this chamber the reduced pressure causes part of the liquid to immediately boil—or flash—into steam. The remaining brine passes through a series of additional chambers (multi-stages) each at successively higher vacuum where the flash process is repeated at progressively lower boiling temperatures."

* * *

Air Pollution

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AIR POLLUTION MENTIONED IN PLATFORMS OF BOTH PARTIES

The following paragraphs are excerpted from published versions of the two Platforms for the 1960 presidential campaign (underlines added). Democratic: "A thin layer of earth, a few inches of rain, and a blanket of air makes human life possible on our planet . . . . Sound public policy must assure that these essential resources will be available to provide the good life for our children and future generations . . . . Water, timber and grazing lands, recreational areas in our parks, shores, forests and wildernesses, energy, minerals, even pure air—all are feeling the press of enormously increased demands of a rapidly growing population." Republican: "We are confronted with major problems in the field of environmental health. We pledge: . . . . Federal authority to identify, after appropriate hearings, air pollution problems and to recommend proposed solutions."

NATIONAL GOALS IN AIR POLLUTION RESEARCH

Following final amendments incorporated at the July 21 meeting of the Ad Hoc Task Group, the long-awaited Report on National Goals in Air Pollution Research is now ready for review by the National Advisory Committee on Community Air Pollution.

AIR POLLUTION EXHIBIT WINS OSTEOPATHS' AWARD

An exhibit prepared by the Air Pollution Programs and displayed at the American Osteopathic Association Convention held at Kansas City July 18-22 was awarded the Association's Certificate of Merit. Approximately 1000 osteopathic physicians attended the Convention.

D. C. HEARING ON PROPOSED NEW AUTO FUMES RULES

At a public hearing in the District Building August 24, witnesses were heard on the proposed new regulations to control auto exhaust fumes in the District of Columbia. They included representatives of the Automobile Manufacturers Association, the American Automobile Association, the D. C. Trucking Association, and the Automobile Exhaust Research Institute, of Cleveland (spokesmen for muffler manufacturers). Several members of the Air Pollution Program attended the hearing as observers and as resource personnel to the District Commissioner.

AIR POLLUTION PROGRAM TO HELP EVALUATE DISTRICT'S CONTROL PLANS

In response to a request from the District of Columbia's Health Department to the Regional office of the Public Health Service at Charlottesville, the Air Pollution Program is undertaking a brief evaluation of the District's control program.

* * *

Nuclear Energy

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SAMPLING STATIONS FOR RADIOACTIVITY IN MILK INCREASED

The Public Health Service announced that since last March it has increased from 10 to 59 the number of sampling stations for measuring radioactivity in milk.

Coverage is now almost nationwide, with at least one sampling station in each of 47 States and the District of Columbia.

Dr. Leroy E. Burney, Surgeon General of the Public Health Service, said that arrangements with the three remaining States—Alabama, North Dakota, and South Dakota—are being discussed with the expectation that all 50 States may be covered by the network in the near future.

Dr. Burney explained that the purpose of the milk-sampling network when it was established in 1957 was to explore the most effective methods for measuring radiation levels in milk.

"Milk was chosen," he said, "since it is among the most important elements in the diet and is constantly available at all seasons and in all climates. A primary objective in the beginning was to develop and simplify methods of collecting and making radio-chemical analyses of milk. Now that better and more economical methods have been developed, it is practical to extend the network. The need to do so became evident when marked differences in radiation levels were found in different parts of the country, indicating that more comprehensive monitoring would be required to assess the radiation exposure of people in all parts of the country."

In the smaller scale operation all laboratory work was done at the Public Health Service Sanitary Engineering Center in Cincinnati, Ohio. The opening by the Service within the past 8 months of two new regional laboratories for radiological analyses, at Las Vegas, Nevada, and Montgomery, Alabama, as well as the experience gained in the prototype milk network made possible the recent expansion.

Under the enlarged system State and local health departments or milk sanitation officials collect samples from major milksheds in accordance with a uniform system and forward them to one of the two new regional laboratories for analysis of radioactive content. The Montgomery facility processes samples from 30 States east of the Mississippi, and the Las Vegas laboratory from States west of the Mississippi.

The milk-sampling stations were located so as to provide for the testing of milk supplied to large population centers across the country. Specially trained employees of cooperating health agencies collect composite samples comprising milk from at least 90 percent of the dairies supplying these population centers and send them to the two laboratories for testing.

Results of the milk tests are tabulated and published in a monthly technical

journal, "Radiological Health Data," published by the Public Health Service. The journal is distributed to scientists, official health agencies, interested members of Congress, and the press. The results of the first analyses made on samples received from the expanded network will appear in the September issue of the journal.

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ASCE-WPCF JOINT SEWER MANUAL ISSUED

A major addition to the ASCE series of Manuals of Engineering Practice is now available in a new volume entitled "Design and Construction of Sanitary and Storm Sewers." Identified as No. 37, this publication is the result of several years of joint effort by the Sanitary Engineering Division of ASCE and the Water Pollution Control Federation (formerly the Federation of Sewage and Industrial Wastes Associations).

The twelve-chapter sewer manual contains 283 pages, over 100 illustrations, 24 tables, and more than 100 references. As the first extended collection of information on the subject, it will make a valuable reference in an important phase of wastewater technology. Individual subjects covered include organization and administration of sewer projects, surveys and investigations, quantity of sanitary sewage and storm water, hydraulics of sewers, design of sewer systems, appurtenances and special structures, materials for sewer construction, structural requirements, construction plans and specifications, construction methods, and pumping stations.

The manual may be ordered with the coupon herewith. The list price is $7.00 per copy. However, ASCE members may order the manual for $3.50 per copy. The price to members of the Water Pollution Control Federation is the same upon application to their organization.

----------CUT HERE----------

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